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**PRELIMINARY
PROCEEDINGS**



**IDENTIFICATION,
EVALUATION, AND
CONTROL OF
TOXIC
SUBSTANCES IN
INDUSTRIAL
EFFLUENTS**



**JUNE 15-16, 1982
CHICAGO, ILLINOIS**

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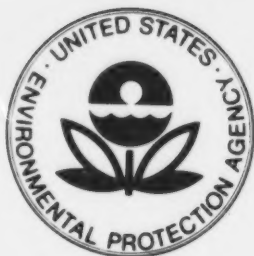
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INTRODUCTION

The Illinois Institute of Technology - Notre Dame Industrial Waste Elimination Research Center is distributing these proceedings. U.S.EPA will be publishing a formal transcript at a later date. The enclosed represents papers as written and provided by the authors.

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The following papers were not available for inclusion at this time.
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INDUSTRY'S NEED FROM REGULATORY AGENCIES
Ray Bodnar, Vice-President, Illinois Chamber
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THE NEED FOR TOXIC CONTROL
Donald Mount, Research Aquatic Biologist,
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INDUSTRIAL LIABILITY - POLLUTION CONTROL FROM
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Henry Maddocks, Account Executive, Alexander
and Alexander

CASE STUDY OF CHEMICAL STRUCTURE/ACTIVITY USE
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Charles Auer and David Klauder, Office of Toxic
Substances, U.S.EPA, Washington, D.C.

OPENING REMARKS BY VALDAS V. ADAMKUS

ADMINISTRATOR, U.S. EPA, REGION V

Workshop on the Identification, Evaluation, and Control of
Toxic Substances in Industrial Effluents

JUNE 15, 1982

Good Morning. I am very pleased to welcome you to Chicago and to our workshop on the identification, evaluation and control of toxic substances in industrial effluents. I am equally pleased that this workshop is being jointly sponsored by the U.S. Department of Commerce, the Illinois Chamber of Commerce and the Illinois Institute of Technology - Notre Dame Industrial Waste Elimination Research Center.

This consortium has produced an agenda for our workshop that has combined developing areas of research with real world implementation needs. I would like to express my thanks to the speakers for the time and effort they have spent in preparing presentations for this workshop.

I would like to express my special thanks to Dr. Patterson of the Illinois Institute of Technology and to EPA's Environmental Research Laboratory staff in Duluth for their assistance in developing this workshop and for assuring the high caliber of the workshop speakers. In particular, I would like to express my appreciation to each of you for your participation here today and tomorrow in this workshop.

It is my continuing belief that the best way to address remaining environmental-human health concerns is through a joint academic-industry-EPA-State-local evaluation program. We need to recognize that there has been significant measurable improvement in the nations waters from pollution control efforts to date. We also need to recognize that industry and municipalities have made substantial progress in restoring full uses to many of our nations



waterways. We also must consider the cost of these improvements and the need to discuss and to determine the most cost effective means of achieving our goals.

Certainly one of the most difficult tasks facing all of us today is the continued progress in protection of the environment without an unreasonable limitation of industrial growth and despite shrinking State and Federal resources. Controlling toxic chemicals in municipal and industrial wastewaters is an important part of this task which poses a significant challenge to industry and to the local, State, and Federal pollution control agencies. We are reminded that hundreds of new chemicals are being produced annually and that many of these chemicals may find their way into our lakes and streams. There is a continuing need to develop ways of controlling toxicants while maintaining the economic strength of American industry. Fortunately, there are ways of dealing with these problems, and our "tools" for doing so are improving. These issues will be addressed here in this workshop.

It is our belief in Region V that many of the industries with direct discharges have resolved nearly all of their water quality problems through construction of treatment facilities or modification of their manufacturing process. While many of the remaining facilities may have implemented pollution control programs, we believe that a more detailed evaluation is needed to determine what additional pollution control for toxicants is needed to meet specific local human health or water quality needs. We want to continue our effort of working with the states and dischargers to lay out and implement a rational systematic program to resolve any remaining problems and that attempts to avoid the panics of the past.

Nationally, U.S. EPA is developing effluent guidelines and water quality criteria to control the discharge of a select number of toxicants of national concern. In addition, U.S. EPA's Regional Offices, the States, and municipalities are now working to implement realistic programs to address facilities which may be of specific local or regional concern because of their particular products, processes, raw material, etc., or to address the unique assemblage of industries in a given river or lake basin. In particular, we have been working with the States to develop and implement a toxicant control strategy that focuses on that 5 percent of facilities which has the highest potential for the discharge of toxicants which may damage human health or the environment.

I am particularly concerned that efforts to control persistent substances be given an extremely high priority in the Great Lakes Basin. I need not recount here the list of these substances which have been found thus far. We continue to find others. As U.S. Co-chairman of the Great Lakes Water Quality Board I am charged with the responsibility for implementing the Water Quality Agreement between the United States and Canada. That agreement calls for increased attention to and vigilance in the control of toxic and persistent substances in the Great Lakes Basin. While we have made and continue to make progress in that area we are obligated to increase our efforts and to ultimately control these discharges. The fact that the Great Lakes also suffer from atmospheric input of many contaminants only increases the need to reduce or eliminate those direct discharges which are most controllable. While there is an absolute need for heavy emphasis on the Great Lakes, we are also aware that significant efforts are needed in our other major basins such as the Ohio and Mississippi River Basins.

I was pleased to observe in the advanced registration list that a number of municipalities are in attendance today along with the anticipated representatives from industry and our state agencies. I believe this attendance is due in large part to the increased awareness by municipalities of the need to adequately define what materials are being or may be discharged into their sewage systems and to determine the fate of these materials in the specific local system and the environment.

As most of you are aware EPA, pursuant to 1972 and 1977 legislation, has adopted national requirements for development of state and local industrial pretreatment programs. Some time before the development of the national regulations the Region through studying the location and type of industry believed there was a need to further evaluate toxicants being discharged to municipal facilities. The main thrust of our Regional pretreatment toxicant control effort aims at the development of strong state and local evaluation/control programs. These programs look at specific local problems such as interference with or damage to the collection and treatment system, violation of receiving stream water quality standards, and contamination of the sludge. To date, the states have identified municipalities where control measures may be needed. These cities need to conduct adequate inventories and evaluations of industries within their system.

While we are here today to look at additional toxicant evaluations that may be justified, we must, as I mentioned previously, recognize the significant water cleanup progress that has been accomplished. In Region V four examples of cleanup progress which are indicative of the total program are:

Ohio River

The Ohio River water quality has shown dramatic improvements in the last 10-15 years. Acid mine drainage, untreated, poorly treated or municipal and industrial wastewaters in the upper reaches with new treatment and controls the densities of fishes in the Upper Ohio increased three-fold between 1957 and 1980, and a number of fish species have returned.

Lake Erie

In the 1960's, Lake Erie was considered to be dying fast due to massive loadings of wastewaters containing oxygen demanding materials and nutrients. Water quality is now improved and, today, the most widely discussed sport fishery in the United States must be lake Erie's Walleyes.

Bay Beach Park - Green Bay, Wisconsin

From 1936 to the late 1970's, Bay Beach, the major beach near Green Bay was closed by bacterial contamination from waste discharges from that city and its industries. Now Bay Beach is once again open for swimming, due to a new well operated municipal waste treatment plant and improved wastewater control by local pulp and paper mills.

Fox River - Wisconsin

The Lower Fox River in Wisconsin was classified as an "industrial river", that was not assumed able to support aquatic life. In the middle of the 1970's, however, the papermills and cities under the states guidance constructed major additional treatment facilities and now the Fox is supporting a greatly expanded aquatic life. Instead of the annual fish kills, the river now has salmon and walleye runs. There is, however, still more work to do in the area of toxicant controls.

The state and industries are now looking at what more needs to be done. There is no question about the river's recreational and aquatic life values and their importance to the economic life of the area.

We are here today to jointly look at what more needs to be accomplished and how we can best focus our limited resources to control those toxicant problems that have the highest potential for damage to human health and/or the environment. I look forward to a productive meeting with you during these next two days and I am hopeful that we can lay the foundation with a scientifically and economically sound toxicant control program. I want to hear from you and work with you not only for these two days, but continuing into the future.

WORKSHOP OVERVIEW BY CHARLES H. SUTFIN
DIRECTOR, WATER DIVISION, U.S. EPA, REGION V
WORKSHOP ON THE IDENTIFICATION, EVALUATION, AND CONTROL OF
TOXIC SUBSTANCES IN INDUSTRIAL EFFLUENTS
JUNE 15, 1982

While there have been a number of national toxicant water quality problems, Region V has been particularly aware of toxicant and other significant water quality problems for sometime because of our experiences on the Great Lakes. We have experienced problems with persistent toxicants such as DDT, PCB, mercury, HCB, etc. Unfortunately, for the most part, we became aware of and reacted to these situations only after they had been identified as major problems. We recognize the need and obligation to the public and to industry to try to surface potential toxicant situations before they become major health or water quality problems. We have been working with our states the last several years to focus our joint efforts on the control of toxic and other significant chemicals. This workshop is part of the continuing dialogue, as in our previous biomonitoring workshop, to interface with industry and to share information on tools that are available to us to address water quality problems and to reduce the cost to industry of any needed evaluations and control measures.

As Val Adamkus mentioned earlier, we recognize that industries and municipalities have implemented pollution abatement programs that, in most cases, have provided major control of conventional pollutants and, directly or coincidentally, some toxic substances as well. For industrial facilities with direct discharges to a waterway, we estimate that about 95 percent do not need further water pollution control improvements to meet national and local requirements. We are now working with the states to focus on the 5 percent or so of the remaining facilities to conduct evaluations and to

determine what, if any, additional controls may be necessary to address local water quality and human health needs.

To focus on toxicant problems, we have redirected our Regional effort. Our previous major effort after the permit program was delegated to the states was reviewing state drafted permits. In late 1980, and early 1981, we met with our states and reoriented our priorities. This resulted in the redirection of the Region's effort to providing technical assistance to the states in the evaluation of the need for toxicant controls. We are now working with the states on a limited number of critical significant permits. This avoids needless paper shuffling and after-the-fact, second guessing. We are also implementing a similar strategy in the pretreatment program where, after an initial training period, federal detailed review is eliminated and total responsibility is delegated to the states for nearly all facilities.

One thing that industry and the regulatory agencies should maintain is public confidence. When several environmental groups heard that we were no longer directly reviewing many of the states permits they became concerned. My staff met with them and explained the logic of jointly working with the states to focus our limited resources on those water quality problems with the highest potential for damage to human health or the environment. We also explained the need to develop responsive state programs where every detailed action was not re-reviewed and duplicated by the Federal government. When faced with the choice of addressing potential significant toxicant problems or of totally assuring that all conventional pollutant limitations were met, the environmental groups agreed with our focus on the smaller number of more critical facilities.

The workshop today and tomorrow is intended to help industry and the regulatory agencies identify potential toxicants which may be released to the environment from a given manufacturing process or activity, and to help evaluate which, if any, of these substances may be of concern. The workshop today has been coordinated with Dr. James Patterson of the Illinois Institute of Technology - Notre Dame Industrial Waste Elimination Research Center and will focus on the identification of toxicants. The workshop tomorrow will focus on the evaluation of toxicity potential and will feature the use of tools developed by the pharmaceutical industry, as well as U.S. EPA's efforts in the field of chemical structure/ activity relationships and their use in predicting persistence, bioaccumulation, aquatic and mammalian toxicity, carcinogenicity, etc. The second day of this workshop has been coordinated with the Agency's Environmental Research Laboratory in Duluth.

PROCESS EVALUATION AND PROCESS MODIFICATION

Two concepts that we will be discussing in detail TODAY are Process Evaluation and Process Modification. They are the head and hands of successful and cost-effective industrial pollution control programs.

Process Evaluation could be called "looking for trouble." Its goal is to identify the sources of potential toxic pollutant discharge problems so that they can be eliminated--ideally, before they occur in the first place. The idea is to gain, within reasonable limits, a complete understanding of the chemicals entering and leaving a given production process, and the routes by which they do so.

Perhaps I should say just a word about why this approach is needed at selected facilities as opposed to simply analyzing the final effluent using a broad

chemical analyses technique. Many toxic pollutants can be of concern even at relatively low levels due to their persistence and ability to bioaccumulate in fish and other organisms. Identifying such chemicals in the final effluent can be difficult due to the low concentrations and possible interferences from or masking by other substances. However, when the search is limited to a particular compound identified from a process evaluation, much lower detection limits are possible. Another factor that must be considered is the batch and seasonal operations of many plants. Samples reflect only the period during which they were collected, whereas a Process Evaluation can look at an entire, typical year of operation on paper. Verification sampling can be designed later to look for a potential pollutant at the proper time and in the proper place.

The first phase of a Process Evaluation does not involve any sampling or chemical analysis. An accurate inventory is compiled of the chemicals associated with the process, including raw materials (together with their known impurities), solvents, catalysts, modifiers, stabilizers, preservatives, cleaning agents, intermediates, products, known byproducts, etc. These data are then combined with basic information on the reaction conditions present at each stage of the process in an attempt to determine whether any additional byproducts could be formed. Consideration must be given to incidental combinations of reactants, for example the mixing of process waste streams, as well as to planned reactions. When potential byproducts have been added to the inventory of process chemicals, the result is a list of all potential pollutants from the process.

The list of potential pollutants then is sorted using available information on environmental significance (such properties as toxicity, persistence,

bioaccumulation factor, etc.) to eliminate those substances known to be of lesser concern. Finally, a monitoring program is designed to confirm the presence or absence of the potential pollutants remaining on the list, and to quantify the discharge of those that are found. Again, the object is to focus on those chemicals that have the highest potential for damage to human health or the local environment and to verify their presence or absence in the discharge.

The second term, Process Modification, is largely self-explanatory. Everyone is familiar with the modifying or tuning of production processes to increase yields, decrease costs, etc. We believe that the concept of Process Modification as a tool for pollution control cannot be overemphasized. Costly end-of-pipe treatment often can be eliminated or greatly reduced through the implementation of a reasonably priced process change. Also, this modification may be a one-time capital cost as opposed to the ongoing operating and maintenance costs of a treatment system, which are subject to inflation.

The simplest modifications involve substituting environmentally innocuous, but functionally equivalent, chemicals for problem pollutants in a process. However, many other attractive alternatives to end-of-pipe treatment are available, and several will be discussed here today. Process evaluation allows industry to be innovative and often saves money while meeting regulatory requirements.

CHEMICAL STRUCTURE/ACTIVITY RELATIONSHIPS

The second day of the workshop will focus upon the use of chemical structure/activity relationships in evaluating a chemical's potential for environmental and human health effects. While we will be mainly discussing the use of structure/activity relationships in evaluating the effects of water pollutants,

the information presented will be applicable to many areas of environmental policy and planning, from the early stages of development of a new chemical to its ultimate disposal in the environment.

During the past 30 years there has been a tremendous growth in the number of chemicals used by our society. There are at least 45,000 chemicals in commerce and that number is growing each year as new chemicals are introduced. Of the hundreds of billions of pounds of chemical compounds that are manufactured each year, a significant amount enters our environment with the potential to adversely affect plant, animal, and human life. Unfortunately, the rapid growth in and variety of chemicals has left us with a large gap in our knowledge about the impact they may have on the environment. In fact, current estimates suggest that less than ten percent of the chemicals in commerce have been adequately tested to determine their environmental fate and biological activity. The resources needed to close this information gap using standard test procedures would be tremendous. For example, the evaluation of the biological effects of a single chemical on a single organism at several different exposure levels would take several years and could cost several hundred thousand dollars. The development of data on environmental fate would likely involve as much time and effort. Given the large number of chemicals already in commerce it is clear that we cannot hope to do a thorough evaluation of all these chemicals. Instead, what is needed is a rapid, cost effective method of predicting environmental fate and biological response. Such a method would make it possible to distinguish those chemicals that are expected to cause adverse effects from those that are of little concern. The limited industrial or regulatory resources available for testing could then be used for the high potential hazardous chemicals. It is because



the area of structure/activity offers such a rapid method of prioritizing the need for testing of existing chemicals that much attention has been focused upon it in recent years. Also, structure/activity provides a tool to assess chemicals presently being discharged as well as the potential effects of new chemicals before they are in the market place and can enter the environment. Both chemical manufacturers and regulators, in particular, U.S. EPA, are at least partially utilizing structure/activity now for both of these purposes, as I will discuss a little later. Although most of the uses of structure/activity have been limited thus far to screening and prioritizing chemicals for testing and regulation, we hope that it will shortly provide a major data base for regulatory decisions on chemicals presently being discharged.

The use of structure/activity in determining biological activity is not a new science. In the nineteenth century it was found that some drugs had certain properties in common, such as water solubility, vapor pressure and partition coefficients. From these observations, it was proposed that the chemical and physical properties of a compound would be extremely important in determining its biological activity. Since this time, much research has gone into predicting biological activity from structure, and this research has been very useful in the development of new pesticides, drugs, and polymers. More recently, environmental scientists have been looking to structure/activity to predict the exposure, fate, and toxicity of chemicals once they enter the environment. Thus far the prediction of physical properties, such as water solubility, water pressure and partition coefficients has been the most successful. These in turn have been useful in assessing environmental fate, for example, in predicting where a chemical will end up such as in water or

sediment and the extent to which chemicals will bioconcentrate in aquatic and other animal life. We will be hearing more about the use of structure/activity in these areas later in the presentations. To date our knowledge about the use of structure/activity in predicting a chemical's toxicity is less developed, in large part, because it is a more complex process and involves an understanding of the way a chemical enters an organism, the paths and chemical changes it undergoes as it travels to an organ and its action at that organ. Even with these limitations, structure/activity has been quite useful in indicating the probable toxicants of certain pesticides and other chemical classes. Again, we will be hearing more about these current uses and projected uses for toxicity estimates by structure/activity in the talks tomorrow.

A goal of this workshop is to present the theory of structure/activity in such a way that you will be able to use it in evaluating the potential environmental effects of the chemicals you deal with. For this reason speakers from various industries will be presenting case histories of the use of structure/activity by their companies. So at this point, I would briefly like to tell you how we at U.S. EPA have been using structure/activity in the regulatory process.

The programs within U.S. EPA where structure/activity has been found to be most developed are those related to the implementation of the Toxic Substances Control Act or TSCA. A good example to illustrate this use is the Premanufacture Review Process under Section 5 of TSCA. Section 5 requires that a manufacturer of a new commercial chemical must notify U.S. EPA at least 90 days in advance of the manufacturing date and must submit certain types of information. Since TSCA doesn't require a manufacturer to conduct

environmental or human health effect assessments on the new chemical, the type of data submitted ranges from a simple chemical structure from one manufacturer to detailed test data from another. Because of the general lack of data, EPA has been using structure/activity techniques to predict the environmental fate and biological effects of these new chemicals. In general, these predictions involve comparing a new chemical to existing chemicals with similar structures for which data bases are available. For example, a manufacturer of a phthalate polymer submitted for premanufacture review was requested to provide more information on this chemical after structure/activity review by EPA. This was done because the new substance was similar in structure to another phthalate which has been strongly indicated to be a carcinogen. Also, because of structural similarities of this new chemical to other phthalates, it was thought that the new chemical might have a high bioconcentration potential and be persistent in the environment.

Structure/activity has also been useful in implementing other Sections of TSCA. The Interagency Testing Committee, formed under Section 4 of TSCA, has used structure/activity in selecting those existing chemicals and classes of chemicals that should be tested for environmental and human health effects. Likewise, structure/activity techniques have played a role in preparation of the first stage risk assessments done under Section 6 of TSCA, i.e., the "Chemical Hazard Information Profiles".

Within U.S. EPA's NPDES Permit Program in Region V, structure/activity has been helpful in selecting facilities that have the potential for toxicant discharges. Both Region V and the States have been prioritizing NPDES dischargers so that those with the highest potential for the discharge of

toxics will be inspected, evaluated and permit limits written, if needed. The inspections include sampling and analyses of waste and/or process streams and effluents for detailed chemical analyses for organics, Ames tests, and biomonitoring of effluents, using fish and Daphnia. The choice of facilities to be inspected has, to a large part, been based upon a facility's processes and the potential to discharge pollutants that are known to be toxic. However, some facilities have also been chosen because they manufacture and/or have the potential to discharge chemicals that may be toxic because they have a structure similar to known toxics. If a facility's discharge does prove to be toxic to fish or Daphnia in the biomonitoring test, or the Ames test is positive, the next step is to find the source of that toxicity.

Structure/activity has proved useful in this step. As an example, a discharger's effluent was toxic to fish but, since over 25 processes were being used, it was not clear which wastestream was the source of toxicity. By using structure/activity, it was possible to predict which waste streams were the source of the toxicity. After biomonitoring of these wastestreams to confirm the predictions, the toxic wastestreams were recycled or disposed of differently, eliminating the toxicity to fish.

Structure/activity relationships can be used by industry and the regulatory agencies as a sorting and screening tool to set priorities for pollution evaluations and to focus on high potential problems. Where a potential pollutant has been identified in an effluent, structure/activity can be utilized to predict toxicity, persistence, bioaccumulation, mutagenicity, etc. Structure/activity can be beneficially utilized as part of a decision tree analysis by industry to identify potentially significant pollution problems and to avoid future liability concerns.

This workshop has been designed to address the identification, evaluation and control of toxicants in municipal and industrial wastewater. The workshop has been designed to further open up the channels between industry and the regulatory agencies so that we may jointly proceed to lay out a reasonable program that addresses the potential discharge of toxicants. I am hopeful that we will all leave here with a better understanding of process evaluation and the advantages of utilizing chemical structure/activity as one of the toxicant sorting tools. I would like you to consider how process evaluation, process modification and chemical structure/activity can be of use to you in your efforts to minimize the impact of your discharge or product on human health and the environment.

Conference on
Identification, Evaluation
and Control of Toxic Substances
in Industrial Effluences

Chicago, Illinois
June 15, 1982

Frederic A. Eidsness, Jr.
Assistant Administrator for Water
U.S. Environmental Protection Agency

Toxic Control: A Regulatory
Perspective

It's a pleasure to be with you today to talk about toxic substances in industrial effluents. It's an important subject which I understand you are tackling from many perspectives. I will address the Agency's specific initiatives on this subject after I give you an idea of where this Administration "is coming from" in general.

When I came to Washington to serve as a member of President Reagan's team, I did so because I firmly believed in this administration's goals. I am convinced that in the past there has been too much intrusion of the federal government into every aspect of American life, uncontrolled government spending, legislation by regulation and solutions to problems that had not even been identified.

One of the best steps to deal with these problems is to transfer appropriate decisions of government closer to those people whom the decisions most directly affect. The Federal government has an important role, but we

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must bring its influence into a more appropriate balance with that of States and localities. At EPA, we plan to accomplish that while carrying out our critical role of environmental protection.

With the President's initiatives of a New Federalism and regulatory reform in mind, I have developed a series of ten principles which I am using to make sure that what we do in the Office of Water fits within the Administration's goals. I have circulated these principles to all of my employees so there is no doubt about what I expect. The President has been quite explicit about his agenda, and I also wanted to be clear about my expectations of how we will do business.

As a first step to reform I want the Office of Water to return to our existing statutory authority and adhere strictly to it. Our basic approach in the past was to write as much into the regulations as was possible. The result of this approach has been a mountain of rules, regulations and guidance which attempted to identify every possible situation that a state or local government or member of the regulated community might find itself in. Then EPA prescribed a remedy for all of them.

As you know, this practice complicated--and in many cases--obscured the basic intent of the environmental laws. We are now trying to go back through these regulations to identify the essential requirements. We are not revising them with a meat cleaver but are carefully going

through them with surgical tools to cut out the fat. We want lean regulations. We want them to demonstrate an attitude that those who read them are at least as intelligent and fair minded as those who wrote them.

I am also stressing the importance of fostering and enhancing debate closest to where the problem exists. I am well aware that Washington is not the center of the universe. There is no way that I can know as much about the water quality of Chicago as the people who live here. It just isn't possible and EPA is not going to be in the business of telling people how to solve all their problems.

What I want us to do instead is to provide States and local governments with enough flexibility to build programs that suit their own characteristics. I hope that giving them that flexibility will stimulate their creativity to find new approaches to old problems.

I'm depending on the creative powers of industry as well, to develop appropriate technology to meet environmental and health standards.

In terms of public health, I want to assure you that I will be promoting those programs where the benefits to society outweigh the costs. At the same time, when a requirement to an industry or municipality is very expensive, the harder we're going to be looking at the scientific evidence behind it. In those situations, we will be sponsoring a thorough debate among peer groups--listening to both those who pollute and those who benefit from the proposed requirements.

That's an idea of the general philosophy I will be carrying out during my term as Assistant Administrator for Water. I'd like to go into some detail about three specific areas that will be of particular interest to you - progress on toxic controls, EPA's second round permitting policy, and a more effective use of water quality standards.

Since I have been at EPA, I have had my belief confirmed that industry wants a tough enforcement program. A good 95% of the regulated community have done their homework and have incorporated environmental controls into their operations. This large percentage wants to do the right thing and to see that others abide by the same guidelines.

Because of their efforts over the last ten years and because of concurrent efforts by municipalities, we have made some very positive changes in the water pollution picture.

Contrary to the Agency's initial concerns that controlling industrial toxic pollutants would involve the addition of unique and expensive treatment systems, we have found that in many cases, well operated and maintained biological and physical-chemical treatment systems can effectively control the discharge of these pollutants. As you know, these treatment systems are presently used by many industrial facilities to comply with BPT limitations.

Although the current BPT discharge limits and existing BPT permits were aimed at controlling conventional pollutants, they are, at the same time, controlling the toxic organics and heavy metals to a significant degree. The

BPT controls on 26 different industries will reduce the direct discharge loading of eight metals between 67% and 93% from the 1972 levels. These figures are remarkable I think. Zinc, for instance will be reduced 93%; lead 92%; copper . . . 91%; mercury . . . 90%.

Of course I realize that since metals are chemical elements, they cannot be destroyed, but the good news is that they are being controlled to this significant degree.

These findings are based on literally thousands of industrial wastewater samples which we have collected as part of our efforts to develop effluent guideline limitations regulations for 34 industry categories. Some of this work was done through cooperative programs with industry. For example, EPA and the Chemical Manufacturer's Association recently completed an indepth sampling program for a selected number of organic compounds in five major organic chemical plants.

Further, through an extensive survey of wastewaters going into and coming out of municipal facilities, we have found that heavy metals are also being reduced through secondary treatment in publicly owned treatment works (POTW). The efficiency of this removal depends on the individual POTW treatment process as well as the concentration of metals.

From 1978 to 1980, EPA's Effluent Guidelines Division conducted a study at 40 POTWs that operated with at least a secondary treatment to determine the fate and occurrence of the 129 priority pollutants. The 40 POTWs were distributed according to size, location, treatment processes used, etc.

The results from this study showed that POTWs meeting secondary treatment requirements provide good removal of priority pollutants -- approximately 67% of the heavy metals, 80% of the total volatile organics and 70% of the total acid-base-neutral organic pollutants. Individually, we can expect a 58% reduction in copper, 65% reduction in chromium, 38% in cadmium and 65% in zinc.

Our statistics on organics are also positive but more difficult to quantify. We estimate that the BPT loadings of total phenols from 26 industries are 94% less than 1972. POTW loadings of total phenol at secondary treatment are roughly 69% less than they were in 1972.

The difficulty in discovering what amount of organic removal we have achieved, lies in a lack of monitoring information. We know that organic compounds in wastewater can attach themselves to solids. They can hydrolyze, volatilize and actually change forms due to chemical reactions during treatment.

Available monitoring data does indicate that BOD reduction almost always results in reducing toxic organic pollutants, but this effect has not been statistically quantified. We know that most biological systems will remove large amounts of certain toxic organics. The overall BOD loadings reductions expected from major point sources from 1972 to full BPT and secondary treatment at POTWs is about 61%.

I don't mean to suggest that our toxic problems are over by any means. If that were true, then you wouldn't be at a meeting like this. The Agency wouldn't be putting out a policy for the Second Round Issuance of NPDES permits for industrial sources or new regulations for water quality standards.

I believe a great challenge facing both EPA and the States is to bridge the enormous gulf between industrial and municipal pollution control regulations and discharge permits which translate these regulations into reality for the individual municipalities and industry.

We know that permits have been written in the past that did not reflect good scientific and economic analysis or were based on regulations that had no adequate peer review and public debate. In other instances, there were no regulations at all.

Permit writers were put in the untenable position of making fundamental public policy, public finance or industry investment decisions without policy oversight, without peer review and without public debate. Our new permitting policy should work toward a solution to this problem, and will do away with permit writers who are, in effect, de facto rule makers.

We have set up five sets of priorities for EPA-issued industrial NPDES permits which I would like go over briefly with you. Although this policy is for EPA permits only, we encourage all States to review the policy and to help us identify those areas where water uses are impaired or other water quality problems exist.

- o The first priority for reissuance of permits will be given to facilities where use impairment problems have been identified and where there is adequate information to develop either a water quality-based permit or in an exceptional case, a BAT/BCT permit relying on best professional judgment.
- o The second priority is to permit facilities which have applicable BAT effluent limitations guidelines.
- o The third priority covers facilities suspected of contributing to the impairment of a designated water use but where insufficient information exists to confirm the extent of that use impairment.
- o The fourth priority addresses facilities for which effluent limitations guidelines are not scheduled for promulgation and the existing permit limitations do not reflect sufficient treatment.
- o The lowest priority is extension or reissuance of permits to facilities for which effluent limitations guidelines are not scheduled and the existing permit requires sufficient treatment.

In carrying out past permitting policy, EPA and States focused almost exclusively on the technology-based effluent limitations approach. While EPA will continue this technology-based approach using BAT/BCT effluent limitations guidelines, the Agency will also be looking beyond technology-based requirements and issue permits based on scientifically determined requirements for assuring environmental protection.

This leads me to our proposed regulations on water quality standards which will be coming out soon. We will be putting an increased emphasis on these standards as part of a natural evolutionary process.

To go back a moment, when the Clean Water Act Amendments were passed in 1972, EPA urged States to adopt ambitious water quality standards. EPA believed that if a fishable use could be obtained within a 20-year period, then the State should adopt that use. Numeric criteria adopted by States usually reflected national criteria set by the EPA. In many cases, the uses and criteria did not reflect the actual physical, chemical and biological characteristics of the stream to which they were applied.

To exacerbate the problem, the EPA adopted as national policy, the so-called Red Book, which contains numeric criteria for a wide range of chemical constituents. The policy argued that such criteria were presumably applicable nationwide and that the burden of proof was on the States to modify those criteria.

State and local governments in recent years, as many of you know, have learned through their own experience that fishable use is not always attainable and the numeric criteria are overly protective of the uses which exist or can be obtained.

A major thrust of our new water quality standards regulations is to provide more discretion for States to adopt or modify uses and criteria to more appropriately reflect the physical, chemical, and biological characteristics of the streams to which they apply. This is not a retreat from environmental

protection but an advance toward use of good science to produce standards and pollution control requirements that will result in measurable water quality improvements that are commensurate with the cost. We want to see where the toxics are. We want to know their actual concentrations, so that we can have effective permits that deal with real problems.

As you will see when the regulations become public, we are returning to the basics regarding water pollution control under States' standards. The basics can be characterized with the following 5 questions:

1. What is the use to be protected?
2. To what extent does pollution contribute to impairment of use?
3. What level of point source control is necessary to restore or enhance the use?
4. What level of nonpoint source control is necessary to restore or enhance the use?
5. Do the benefits bear a reasonable relationship to the cost?

These questions will be answered in a public process with peer review. In an open forum, all interested parties will have an opportunity for involvement in selecting priority water bodies, collecting data and arriving at standards revisions.

You may have concerns about the resource implication of revising standards along these lines. Without a doubt, there will be an increased need for local site specific analyses in order to focus on priority problems. I am convinced that this is an area where the state/local partnership role

envisioned by the CWA should be intensified. I am also convinced that those of you in the regulated community will be more than willing to bear a fair share of developing monitoring data, analysis and information necessary to revise standards. It will be your self interest to do so as we go forward in our efforts on toxic control. No elected official or industry wants to make an investment control decision unless it is well founded in scientific bases and has public support.

As the water quality standards regulations go through development, an even greater challenge faces the new leadership efforts in revising water quality standards. A basic strategy which we intend to employ is that EPA will conduct general reviews of submitted State water quality standards and will only become involved in detail reviews where our scientists and engineers feel that there is substantial uncertainty about the States' methodology for modifying uses or criteria. We believe that the combined effect of the change in the water quality standards regulations, technical guidance which will accompany the regulation, and this new EPA oversight strategy, will give the states meaningful primary responsibility over this important aspect of the Clean Water Act.

The next few years are important ones as we implement the new programs which will deal with toxic control, such as second round permitting and water quality standards. What happens next is up to people like you. It is critical that we pitch in together to make these initiatives work--because if we don't . . . you can bet we'll end up with even stronger federal legislation in ten year's time.

You have a heavy schedule ahead of you today and tomorrow. I know it will be time well spent as you discuss some very difficult subjects. Good luck to you.

**WORKSHOP ON
THE IDENTIFICATION, EVALUATION, AND CONTROL
OF TOXIC SUBSTANCES IN INDUSTRIAL EFFLUENTS**

**Chicago, Illinois
June 15, 1982**

**Wayne Nichols
Director, Ohio EPA**

Ohio's Toxicant Evaluation/Control Strategy

BACKGROUND

Presently, the majority of NPDES Permits issued to municipal and industrial dischargers have either expired and have not been re-issued, or have been re-issued with a continuation of effluent limitations that were originally required to be achieved by July 1, 1977. For industrial dischargers, these initial permits were required to contain effluent limits based upon the application of "best practicable control technology currently available" (BPT), as defined by Federal regulations promulgated pursuant to Sections 301 and 304 of the Clean Water Act (CWA, PL 95-217). For municipal dischargers, the achievement of secondary treatment, as defined by the regulations, was required. Where these technology based limits were insufficient to ensure the maintenance of Ohio Water Quality Standards, a more restrictive effluent limit was incorporated into the permit based on those Standards. The Clean Water Act further requires that industrial dischargers achieve effluent limitations reflecting "best conventional pollutant control technology" (BCT) for biochemical oxygen demand (BOD), suspended solids, pH, fecal coliform bacteria, and oil and grease by July 1, 1984. All other pollutants must be treated to a level consistent with the application of "best available technology economically achievable" (BAT).

The U.S. Environmental Protection Agency has promulgated only two technology based effluent guidelines (Timber Products Processing and the Steel Industry) and has proposed guidelines for several other industrial categories containing BAT/BCT requirements. There have been no proposed regulations defining "best practicable waste treatment technology" for municipalities. It is unlikely that the Ohio EPA will be able to issue permits derived from federally defined BAT/BCT technology based effluent guidelines in the near future. For these reasons, the Ohio EPA will issue the next round of permits based upon Ohio Water Quality Standards and the application of best professional judgement (BPJ) to determine maximum control technologies for the control of toxic parameters to achieve water quality standards.

The establishment of state water quality standards is a highly complex process. Its purpose is to insure that the desired use for a given water body is protected by establishing appropriate narrative statements or numerical limits for specific contaminants.

The two major components of water quality standards are:

1. A designated beneficial use, or uses, and
2. Narrative statements and numerical limits for specific contaminants to protect the designated use.

There are a number of possible beneficial uses for a water course. These include; public, industrial, and agricultural water supply; livestock and wildlife watering; aquatic life; bathing waters; and boating, canoeing and esthetic enjoyment.

Once a designated beneficial use is established, numerical limits and narrative statements are set to protect that use. These limits may either provide a high level, moderate level, or low level of protection.

Water Quality Criteria can most simply be defined as scientific judgements about the concentration of water constituents which, if not exceeded, are expected to be protective of a water use. Criteria may also be narrative statements. They provide scientific guidances for the standards setting process, but they do not have direct regulatory impact.

With that background in mind, let me briefly outline some of the current thinking, procedures, and problems facing Ohio and other states in the development of a Water Quality Standards Program.

USE ATTAINABILITY

The two most frequent criticisms of a water quality standards program are:

1. Stream uses have often been set without an adequate analysis of whether or not they were attainable; environmental, technological and economic constraints that might preclude the attainment of the desired use were seldom considered;
2. Criteria established to protect uses have sometimes been overly restrictive; they did not take all available scientific data into account; and they were not responsive to site specific variations in water quality, such as physical, chemical and biological factors that might affect either the attainability of the use, or the criteria necessary to support the attainable use(s).

SEGMENT SPECIFIC WATER QUALITY STANDARDS PROCESS

Stream segment specific water quality standards are established by determining the appropriate use classification and identifying water quality criteria capable of achieving that use. Once established, these standards are translated into NPDES effluent limitations by the wasteload allocation process. The Ohio Water Quality Standards that were adopted on February 14, 1978, established standards for all surface waters in the State. However, the Ohio EPA is concerned that these standards do not accurately reflect the attainable use(s) of some water bodies, and, if applied without re-evaluation, may require more or less stringent wastewater treatment than is really needed to meet the goals of the Clean Water Act. Therefore, existing stream use classification and associated criteria are being re-assessed during the water quality standard setting/wasteload allocation process, and NPDES Permits are being issued only after the process is completed.

The methodology developed by Ohio for determining use attainability contains 4 major steps:

1. An environmental assessment,
2. A wasteload allocation,
3. An economic evaluation, and
4. Public hearings.

The re-assessment process begins with a desk-top review of the stream use established in the 1978 standards. In the absence of evidence to suggest otherwise, the 1978 stream use(s) will remain effective. The Ohio EPA will perform a stream use attainability study in cases where valid concerns about the attainable stream use(s) are raised. The Ohio EPA has developed an initial list of streams where a thorough evaluation of stream use is needed. Where data are insufficient or lacking for a through "desk top" review, intensive stream surveys must be conducted.

Biological, physical, chemical, socioeconomic and technological factors must be considered when evaluating use attainability. In Ohio, proposed aquatic life stream use is formulated based upon biological criteria, existing chemical/physical conditions, and an examination of the limiting factors preventing the establishment of aquatic communities that might otherwise be present in a system.

Biological assessments are fundamental to measuring the biological health or integrity of aquatic ecosystems. Surrogate approaches to assessment, such as measuring the physical and chemical characteristics of the water column simply cannot be used with certainty to predict whether or not biological integrity exists. Our current state of knowledge does not allow us to accurately predict biological communities based upon physical and chemical measurements alone. The best indicators of the environmental conditions generally suitable or unsuitable for the existence of healthy and well-balanced aquatic communities are the organisms themselves.

Ohio uses fish and macroinvertebrates in making biological assessments in streams. Key components include: species richness, species diversity, relative abundance, abundance of sensitive or intolerant species, abundance of pollution tolerant species and, in the case of fish, external symptoms of disease, size and weight, presence and abundance of obvious hybrids, and an index of community well being.

In ideal cases, an entire sub-basin is evaluated so that the biological condition of a particular stream segment can be compared with the condition of other stream segments within a watershed. When minimally disturbed reaches cannot be found in a study area, similar stream segments from adjacent drainage basins are used for control streams. Stream and effluent sampling are conducted concurrently to evaluate the physical/chemical water quality of the stream and wastewater entering the stream.

A factor that is equally important to physical/chemical water quality and its affect on the biological community is the physical characteristic of the watershed and stream channel. What is the prevailing land use; pasture, row crop, orchard, forest, or urban? Has the stream channel been modified? What is the predominant substrate, channel depth, stream velocity, and stream bank vegetation? Is the canopy open or closed?

Once the environmental assessment has been completed, the data are evaluated and a stream use is recommended. Data collected during the environmental assessment are used for developing a recommended wasteload allocation based upon the stream use assigned.

Water quality standards are translated into NPDES effluent limitations by the wasteload allocation process. Wasteload allocations are calculated by either a mass balance equation or a time-decay equation. Wasteload allocations done for non-conservative substances (i.e., substances that are subject to biochemical oxidation or other processes that cause them to decay with time) are calculated by utilizing a mathematical stream model. The model can predict stream quality when it is calibrated and verified by using actual ambient stream conditions. Mass balance or dilution calculations are used to predict stream quality for conservative substances (i.e., substances that do not decay with time). The critical dry weather flow most commonly used in stream modeling is the 7 day, 10 year low flow. Increasingly higher stream flows of specified duration can be used to model in-stream water quality within the segment. The resulting allocated discharge limits for each flow can then be tabulated and proposed for use as "tiered" permit limitations for certain chemical parameters. The degree of complexity in this analysis will depend upon the nature of the stream segment. For example, wasteload allocations that involve discharges into lakes or estuaries often require very complex mathematical modeling.

Based upon the effluent limits used to achieve the standard, the Ohio EPA will complete the attainability analysis by making the following determinations.

1. Is it technologically feasible to meet the effluent limits, and if not, what human health or environmental harm will be associated with a less stringent limitation? For example, it is Ohio EPA policy that the best effluent limits realistically attainable for municipal wastewater treatment facilities with current technologies is 10 mg/l BOD, 12 mg/l suspended solids, and 2.0 to 1.5 mg/l ammonia. If the effluent limits are technologically attainable, the analysis proceeds.
2. Is it economically reasonable for the discharger to build, maintain, and operate the facility needed to achieve the effluent limits? For municipalities, this is part of the facilities planning process and the development of advanced treatment justifications; for industries, it is necessary to determine if the required wastewater treatment facility can be constructed and operated without causing severe economic impacts.

ECONOMIC ATTAINABILITY

The economic attainability of the proposed stream use is also an integral part of the overall evaluation process. For industrial dischargers, this is not easily defined. Obviously, a plant closure would be an adverse economic impact. For municipalities, benchmarks have been established for reasonable user charges. These benchmarks are related to the disposable income of the community after essential expenses have been paid. When economic costs are judged to be excessive, the level of protection can be modified for specific parameters within a use, or the use designation may be dropped and a different use established.

If a specific limit is attainable from a biological and economic standpoint, these limits will be incorporated in the appropriate NPDES Permit. Public hearings are held on the proposed stream uses and wasteload allocation. The stream standards are either adopted or re-evaluated based upon the input

received at the public hearing. The Ohio EPA may consider modifying the standards for a particular segment in order to arrive at attainable limits wherever the proposed effluent limit is unattainable either due to technological reasons, undue economic hardship on the users of publically owned treatment works, or severe economic impacts on industrial facilities. A modification to the standards or effluent limits may be done in one of the following ways.

1. The establishment of a seasonal use designation where the criteria vary from one period of the year to another.
2. A modification of the level of protection by having less stringent criteria for certain parameters but retain the same general use designation.
3. Issue variances for specific discharger(s) that delay the imposition of more stringent effluent limitations on the parameter(s) that exceed water quality standards criteria.
4. Issue "tiered permits" that specify variable loadings of pollutants that are contingent upon measured in-stream flow volume (also referred to as flow variable permits).
5. Remove the present designated use and evaluate the next lower use designation.

Modifications to the water quality standards or the effluent limits will be made only to the extent necessary to achieve the stream use(s) or effluent limits that are deemed attainable by the Ohio EPA. An action to modify a water quality standard is subject to the "Antidegradation Policy" set forth in the Ohio Water Quality Standards and is subject to review by U.S. EPA.

The entire process generally takes from 1 to 3 years. The data collection, analysis and report preparation is a 6 to 18 month process; the preparation of standards for public hearings, the hearing, and the adoption process takes a similar length of time.

PERMITS BASED ON THE GENERAL STANDARDS AND BEST PROFESSIONAL JUDGEMENT (BPJ)

In those instances where the Ohio EPA has identified significant discharges that may be harmful to human, animal, or aquatic life, or that may cause taste and odor problems, and which are not addressed by stream segment specific water quality standards, the Ohio EPA intends to proceed to develop effluent limitations according to the principles and procedures set forth in this section. Pollutants for which these procedures are applicable do not have numeric criteria listed in water quality standards of the Ohio Administrative Code. The development of NPDES Permit limits for such pollutants will be related to specific dischargers and will be done on a case-by-case basis. Industrial discharges in the first round of permitting were generally regulated on the basis of the application of BPT control technologies and water quality standards. It is anticipated that some Federal guidelines will be promulgated to define BAT and BCT technologies for certain of the commonly identified pollutants such as BOD, suspended solids, and some acutely toxic pollutants such as ammonia, chlorine, and heavy metals.

However, it is unlikely that Federal guidelines will address more than a small number of toxic pollutants. Therefore, in the absence of Federal guidelines for toxic pollutants, notably those that are acutely or chronically toxic, persist or bioaccumulate in the environment, or are carcinogenic, mutagenic or teratogenic, the State General Standards will be the legal basis for permit limitations. The following procedures will be employed in the development of permits based upon water quality standards and best professional judgement (BPJ) for those facilities known or suspected to have toxic or other significant pollutants in their discharge.

- 1 The Ohio EPA will develop a prioritized list of industrial facilities with known or suspected toxic pollutant discharges that will receive first priority for NPDES Permit re-issuance. Industrial dischargers with no known or suspected toxic parameters in their discharge would receive a lower priority for permit issuance.
- 2 For each facility on this list, the Ohio EPA, in consultation with the facility, will identify the specific parameters known or suspected to be present in the facility's discharge.
- 3 For each known or suspected toxic pollutant, there will be a determination by the Ohio EPA as to whether sufficient information is available to develop specific permit limits.
4. Where it is believed that toxicants are being discharged but inadequate information is available on effluent constituents or concentrations, the Ohio EPA may require a permittee to either conduct a process evaluation, or to monitor for the presence of the toxicant rather than impose an effluent limitation with inadequate justification. (This monitoring will only be for a limited period depending on the effluent variability.)
5. The Ohio EPA will apply best professional judgement to determine maximum control technologies where generally accepted scientific information has confirmed the presence of acutely or chronically toxic substances, persistent or bioaccumulating toxic pollutants, or probable carcinogens, mutagens, or teratogens in concentrations that are harmful or present unacceptable health risks. Maximum control technology should not be confused with BAT, as currently defined by the U.S. EPA. The assessment of water quality problems and the exercise of professional judgement in determining maximum control technologies will be based on the following principles.
 - a. Effluents should not be acutely toxic or chronically toxic to aquatic life.
 - b. Effluents should not contain bioaccumulative substances in concentrations that may be accumulated to levels harmful to humans, animals, or aquatic life.
 - c. Carcinogenic, mutagenic, or teratogenic compounds in the effluent should be reduced to an acceptable risk level which will be determined by the Ohio EPA and may be developed on a case-by-case basis. Wherever technological and/or economic considerations preclude elimination of such risks, maximum control technologies will be such that an acceptable risk level is achieved. Future reductions in risk level will be dependent upon technological and economic considerations.

- d. Any toxic pollutant(s) identified in an effluent in amounts which present overriding environmental or human health threats will require corrective action irrespective of economic impacts.
6. Throughout the process of developing permit limitations and self-monitoring programs, the Ohio EPA intends to work closely with individual dischargers to develop the necessary information to perform an attainability analysis with regard to each specific limit.
7. Once the permit has been drafted and the limits determined to be attainable, the Ohio EPA will initiate public notice and administrative proceedings necessary to issue the permit.

The Ohio EPA believes that this analysis is more appropriate on a permit-by-permit basis where limitations are based upon the General Standards rather than developing State-wide criteria as is the case for segment specific standards.

The Ohio EPA intends to utilize a variety of sources of information to assess water quality problems and the technical and economical feasibility of the appropriate limitation for a toxic pollutant. Federal water quality criteria documents and published scientific literature will be consulted when assessing the human health risks and the toxicity to aquatic life of specific substances. The Ohio EPA also intends to discuss options with the permittee with regard to the availability of alternate raw materials and process changes, recycle or selective waste stream treatment, and "best management practices" to minimize the discharge of these substances. In each instance where the Ohio EPA proposes effluent limitations based upon the General Standards, it will be necessary to document the need for those limitations. In doing so, the Ohio EPA intends to rely on information presented in the public proceedings associated with permit development and issuance, including recommendations by the permittee.

FORMULATING BETTER WORKING RELATIONSHIPS

I believe a key factor in the success or failure of water quality standards in obtaining the desired goals of environmental protection at a reasonable cost will be the working relationships between the states and the federal government, as well as local governments, private industry, the scientific community and, last but not least, the public affected.

A partnership, whereby, we work together for common goals and pool our resources so that we have the facts necessary to make intelligent choices will be essential for success. No longer should adversary roles be the rule. Too many resources are wasted at the expense of us all, including the environment upon which we depend.

In the final analysis, the process of setting appropriate risk levels will probably be a political decision rather than a scientific one. The key questions being what do we the public want and how much are we willing to pay?

Process Evaluation for Identification of Potential Toxicant Problems

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The historical and still prevalent approach to industrial pollution control has been end-of-pipe treatment, and discharge of the treated effluent. This approach has been encouraged by both regulatory efforts and by the relatively modest costs (typically \$0.50-\$2.00/1000 gallons) to industry of wastewater treatment. Although many end-of-pipe industrial wastewater treatment facilities produce treatment sludges with toxic properties, the cost of disposal of these residue was, until recently, negligible.

This historical end-of-pipe approach was developed to control conventional pollutants such as biochemical oxygen demand (BOD) and suspended solids and in most instances remains valid for control of such conventional pollutants today. However, today we are also concerned with the identification and control of a wide spectrum of toxicants, and new approaches and methodologies must be considered.

Individual toxicants in an industrial effluent may result from a number of sources, including the following:

- Raw material or manufacturing additive, which is lost from the manufacturing process;
- A toxicant's presence as a contaminant in a raw material;
- Manufactured product, which is lost from the manufacturing process; or
- Side reactants generated in the manufacturing process, and extracted in a product purification step.

When attention is focused upon the point of generation of an individual waste stream within a manufacturing facility, and the spectrum of pollutant sources identified above are considered, it becomes simple to perform process evaluations which predict by source the potential occurrence of toxicants. Confirmatory monitoring is normally necessary, however.

Such a process evaluation normally incorporates the following five aspects:

1. An examination of all process related chemicals, including their impurities.
2. An investigation and dissection of the manufacturing processes, to identify all operations and chemicals present, and the physical and chemical conditions imposed at each step.
3. Determination or deduction of possible chemical by-products formed in each of the processing steps.
4. A preliminary estimation, based upon readily available information, of the potential of the known and suspected chemicals to harm human health or the environment.
5. Development of a monitoring scheme to verify the presence or absence of the suspected chemicals of concern in the facility process effluents, and to determine pollutant concentrations.

We have performed several such industrial process evaluations, often with unexpected but successful results. For example, we recently evaluated one relatively small organic chemical facility, which utilizes a limited array of raw materials and processes, to synthesize one primary product, and to formulate five additional products based upon the primary synthesized product plus other formulation chemicals. Our study identified 49 known or suspected organic contaminants including several priority pollutants. Perhaps the most important contribution of such a study is the recognition that the number of potential pollutants associated with even a simple manufacturing facility may exceed by several fold the number of pollutants suggested by a cursory examination.

In a second study, a large facility synthesizing two products via a complex series of chemical reactions was evaluated. Over 75 process related pollutants were predicted, again including numerous priority pollutants. A key point to note here is that while such an evaluation may predict the presence of a pollutant, it is more difficult to accurately predict the concentration at which that pollutant will occur. This uncertainty reinforces the need for confirmatory monitoring.

Following the identification of, and determination of the need for control of a toxicant, the conventional following step involves the implementation of some type of pollution control technology. This technology, which is usually end-of-pipe, involves the expenditure of capital and operating costs for abatement.

An alternative to end-of-pipe treatment is in-plant production management, to avoid or reduce the generation and discharge of pollutants, by efforts such as the following:

- Change in raw materials
- Modifications to manufacturing processes
- Adoption of new, non-polluting manufacturing technologies
- Resource recovery from process solutions and wastestreams

Although this alternative of in-plant management has been generally perceived as a desirable conceptual approach, it has typically been given only lip service by both regulatory authorities and industry, with some notable exceptions. In these exceptional cases, the motivation to shift to in-plant management has been primarily economic, and not regulatory. The economic impetus has resulted when the total value of resources recovered, plus pollution control costs avoided, represented a profit to the implementing industry. Notable examples include solvent and spent oil recovery, as well as limited instances of recovery of valuable metals (silver, gold, copper) from certain plating or metal refinery operations. Nevertheless, the advances in in-plant management have been quite modest, and always with economics as the driving force.

One of the best publicized and perhaps most successful industrial programs of in-plant pollution management was initiated in 1975 by the 3M Company. The program was established to help reduce the amount of resources, manpower and money necessary to comply with environmental laws and regulations.

The program is aimed at avoidance of conventional end-of-pipe or top-of-stack pollution control, and each authorized project must meet four criteria:

1. It must eliminate or reduce a pollutant that is a problem or a potential problem
2. It should result in improved use of energy, raw materials or other resources.
3. It should incorporate a technical accomplishment, innovative approach, or unique design.
4. The accomplishment must have some monetary benefit.

During the first six years of this program, 3M has reported monetary savings in excess of \$90 million dollars, on 545 projects in 20 countries. This is in addition to the pollution avoidance accomplished.

Pragmatically, an economic driving force will always be the principal incentive for industry to turn to alternatives to classical end-of-pipe treatment. However, recent events have resulted in a dramatic change in these economics. Specifically, these factors are the escalating costs of raw materials and products, plus the rapidly escalating costs and limited opportunities to dispose of hazardous waste residues constituting both spent process chemicals (solvents, acids, etc.) and toxic sludges from end-of-pipe treatment. Depending upon the industry and disposal point locations, and the nature of the hazardous wastes, hazardous waste disposal costs for drummed wastes of \$2.00-\$10.00/gallon are not unusual. Since industrial treatment plants typically produce 1-10 gallons of residue per 1,000 gallons of wastewater treated, the net effect of the escalation in hazardous wastes disposal costs has been to increase overall treatment and disposal costs by factors of 2 to 200-fold.

This economic stimulus has resulted in an emerging and rapidly expanding industry interest in opportunities for, and technologies and economics of in-plant management to reduce or avoid the need for end-of-pipe treatment. In consequence, I suggest that with this economic impetus, the timing is right for industry to begin to shift from a conventional treatment approach to the alternative of in-plant process evaluation, and toxicant contaminant, avoidance or reduction, or recovery. This shift will require the coordination of industrial process engineering with the skills of environmental engineering.

Although some technologies are already available to achieve in-plant control or recovery and others are in the development stage, there is still much research and development required to support a major shift to in-plant management. Some examples of recently emergent technologies include the following. In the petroleum refinery industry, a patented process has recently been developed to rejuvenate for reuse spent caustic from refinery desulfurization. As another example, Chevron has developed a new catalytic-cracking catalyst which reduces SO₂ emissions by more than 80%. Goodyear has patented a process which destroys PCB's in contaminated heat-transfer fluids, thereby allowing the subsequent recovery of the fluids for reuse. These examples represent only a few of the spectrum of opportunities available. Many others are cited in the recent United Nations Environmental Program publication, Low- or Non-Pollution Technology Through Pollution Prevention.

I would like to describe for you today a recently established research center, involving a partnership between the Illinois Institute of Technology, the University of Notre Dame, and the U.S. Environmental Protection Agency. This is the Industrial Waste Elimination Research Center, headquartered at the Illinois Institute of Technology. The Center was established under the U.S. EPA "Centers of Excellence" Program. That Program was organized by the U.S. EPA as a response to Congressional concern that the EPA was not adequately supporting long-term and fundamental environmental research, and was initiated in 1979.

Under this program, the EPA identified eight broad areas of environmental research which were to be focused in these Centers of Excellence, and through competitive procedures selected an institution or consortium of institutions to establish and man a research center involving each research area. Three Centers were established in 1979; four Centers in 1980; and one additional Center in 1981.

Three of the Centers are "technology-based" centers. These are the Advanced Environmental Control Technology Research Center (AECTRC) at the University of Illinois at Urbana, established in 1979; the Industrial Waste Elimination Research Center (IWERC) established in 1980; and the Hazardous Waste Research Center (HWRC) established in 1981 at Louisiana State University. Briefly, the mission of AECTRC is end-of-pipe control technology. IWERC activities are directed to in-plant control, and the Hazardous Waste Research Center is concerned with off-site disposal, destruction and containment of hazardous wastes. I will direct the remainder of my comments to

the Industrial Waste Elimination Research, for which I serve as Director.

The mission of IWERC is fundamental and exploratory research on industrial waste elimination, reduction, or avoidance, by recovery, recycle/reuse, and other methods of in-plant management. The researchers of the Center include university faculty, post-doctoral and visiting scientists, and graduate students, representing about equally environmental and chemical engineers.

The organization of the Center includes a Policy Board, which oversees the Center programs. I report as Center Director to the Policy Board. We have two advisory groups, consisting of off-campus representatives. These are the Industry Advisory Council and the Scientific Advisory Committee. Reporting to me, and responsible for the research activities performed on the two consortium member campuses, are institutional program managers.

The Policy Board consists of senior level EPA officials, plus myself and the Directors of the other two technology research centers. The EPA representative to the Policy Board include both ORD and other programmatic offices. The responsibilities of the Policy Board include the establishment of broad policy directions relating to the mission of the Center, and review of the operation and achievements of the Center with respect to its mission and objectives. Although the Policy Board selects general research areas of high priority, it does not select or designate specific research projects. This function is performed by the Center Director, in consultation with his advisory groups and Center researchers.

As mentioned earlier, I serve as the Center Director. As such, I direct the day-to-day operations of the Center, serve as the point of contact between the Center, its host universities, and the outside world, and promote the goals and programs of the Center. Our two institutional program managers are Dr. Ken Noll at IIT, and Dr. Tom Theis at Notre Dame. These individuals assist me in the administration of the Center, and monitor individual projects located on their respective campuses.

Our Industry Advisory Council performs several key functions, including liaison between the Center and industry, and providing industry perspective. They assist in promoting cooperative programs between industry and IWERC, and help us to establish mechanisms for industry review and transfer of IWERC research results. With respect to the membership, representatives are selected from major industrial groups. Qualifications

include policy-level corporate responsibilities, and involvement with environmental issues at the national level, typically through industry associations. The current membership includes representatives from most major categories of industry.

The Scientific Advisory Committee serves a quality control function with regard to research proposals, research projects, and research reports. The members are nationally prominent engineers and scientists, and serve one-year terms with eligibility for reappointment. Representatives are from industry, other universities, and government research laboratories.

This year, the Center anticipates EPA funding of \$750,000, up 50% from last year. In addition, some industry funding has been awarded. We anticipate that with time, the non-EPA funding from industry and other federal, state and local agencies will expand to match the EPA funding.

We are currently focussing our efforts in six major research areas, although we expect to expand this coverage as our funding levels increase. These six areas of research are:

- Metals speciation and separation
- Sorption/desorption phenomena
- Particle size and shape conditioning
- Anaerobic process application/control
- Membrane separation processes
- Catalysis

On January 1, 1981 we initiated four major lines of research associated with the first two listed research areas, and a fifth project concerned with anaerobic detoxication of concentrated process wastes. A fifth project, on liquid-liquid membrane extraction for metals recovery was initiated in March.

In closing, I would like to note that IWERC is not the only organization involved in research and development on process evaluation and in-plant management technologies. As suggested earlier by the few examples which I cited, some industries are also active.

The Center however can address generic rather than site-specific opportunities and, I believe, has the opportunity and capabilities to achieve significant advances in the state-of-the-art of process evaluation and in-plant management for industrial pollution control.

EPA WORKSHOP

**IDENTIFICATION, EVALUATION, AND CONTROL
OF TOXIC SUBSTANCES IN INDUSTRIAL EFFLUENTS**

**JUNE 15-16, 1982
CHICAGO, ILLINOIS**

INDUSTRIAL PROCESS MODIFICATION FOR TOXICANT CONTROL

by

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ABSTRACT

A study is presented on various chemical industries to determine the sources of toxicant production and to suggest possible process modifications to minimize or eliminate the toxicant. The industries which are examined include pyrometallurgical and hydrometallurgical processing of ores; electroplating, coal liquification and coal gasification. Flow diagrams indicating the source of the toxicant in the process and flow diagrams suggesting process modification to eliminate the toxicant are presented. For each process, suggested research areas to provide additional knowledge to execute the modifications are proposed.

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INTRODUCTION

Terminal treatment of industrial toxicants has been the dominant method of pollution abatement, but these toxicants can be reduced more efficiently through process modification. An extensive study was conducted for the Industrial Waste Elimination Research Center, IWERC, of Illinois Institute of Technology and Notre Dame [1] to evaluate various processes in the chemical process industry to determine process modifications which would minimize or eliminate toxicants. From this study specific research directions were suggested for future research to be conducted by IWERC. Towards this objective, it is not necessary to generate detailed descriptions of the process or the modifications. Rather, the sources of pollutants within the processes are determined and modifications are suggested which will have significant impact on toxicant elimination. Although the industries examined are diverse, research areas for study can be identified which are generic in nature and which can impact positively on toxicant elimination through the process modifications suggested. The industries examined in the report [1] are (a) Refining of Nonferrous Metals, (b) Electroplating of Common Metals, (c) Coal Conversion Processes, (d) Explosives Industry, (e) Primary Aluminum Industry, and (f) Phosphate Fertilizer Industry. In this paper, toxicant problems will be highlighted in the processes of (a) Pyrometallurgical Processing of Copper, (b) Hydrometallurgical Processing of Copper, (c) Coal Liquifaction, and (d) Coal Gasification. From these studies various process modification strategies and attendant research

programs which will minimize these toxicants and are generic in nature are identified.

PYROMETALLURGICAL PROCESSING OF COPPER

Ninety percent of the world's primary copper originates in the sulphide form. A vast majority of this copper is extracted by pyrometallurgical techniques because sulphide ores are not easily leached. Typical copper deposits contain only 1 to 2% copper. The ore must undergo several process steps to concentrate the copper before smelting. This method of copper extraction includes the following steps [2]:

1. Concentration by Froth Flotation
2. Roasting
3. Matte Smelting
4. Converting to blister copper
5. Electrowinning

The pollutants of primary concern include SO_2 , particulates, slag, and dissolved metal salts in various effluent streams [3]. Figure 1 is a flow chart of this process, indicating the numerous ways in which concentrate can be smelted to produce blister copper.

Other sources of waste water include acid plant blow-down, slag granulation, and cooling of the hot metal anodes. Electrowinning also generates waste through spent electrolyte, washing cathodes, and the recovery of slime [4].

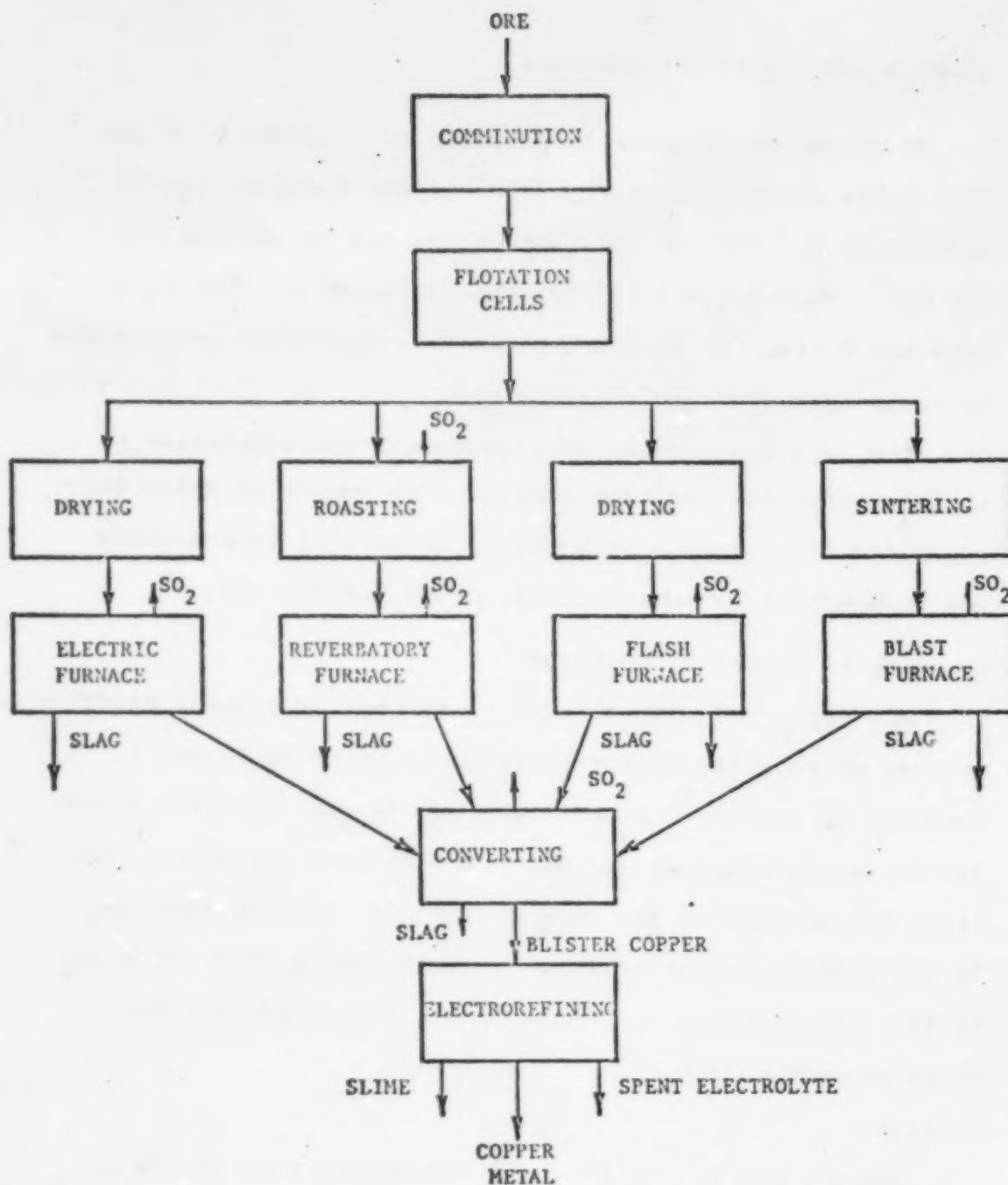


Fig. 1: Flow Chart showing the principal process steps for extracting copper from sulphide ores. [2, pg. 2]



Comminution and Froth Flotation

A copper concentrate is produced by a series of flotation cells which selectively float copper sulphide to the surface of the bath so the concentrate can be skimmed off the top. This process is depicted in Figure 2. The tailings taken from the tank are piped to evaporation ponds where water is clarified and recycled [5].

The tailings require pH adjustments and extraction of arsenic, cyanide, and some metals. The amount of water consumed for this process step can be reduced if improvements are made of the grinding efficiency of the dry ore.

Roasting of Copper Concentrate

The copper concentrate can be refined by several different methods of roasting and/or smelting as shown in Figure 1.

Roasting of sulphide concentrates produce calcines for leaching or for reverberatory (or electric) furnace smelting. The fluid-bed roaster is the best device for sulphide roasting. It has a high production rate and it produces 5-15 vol.% SO_2 in the flue gases which can be easily converted into usable forms of sulfur [6].

Smelting

The process of smelting and converting vary widely in equipment design but the pollutants are essentially the same: SO_2 , particulates, and slag. There are several reasons for cleaning gases from metallurgical processing; the most important of these are [6, pg. 296]:

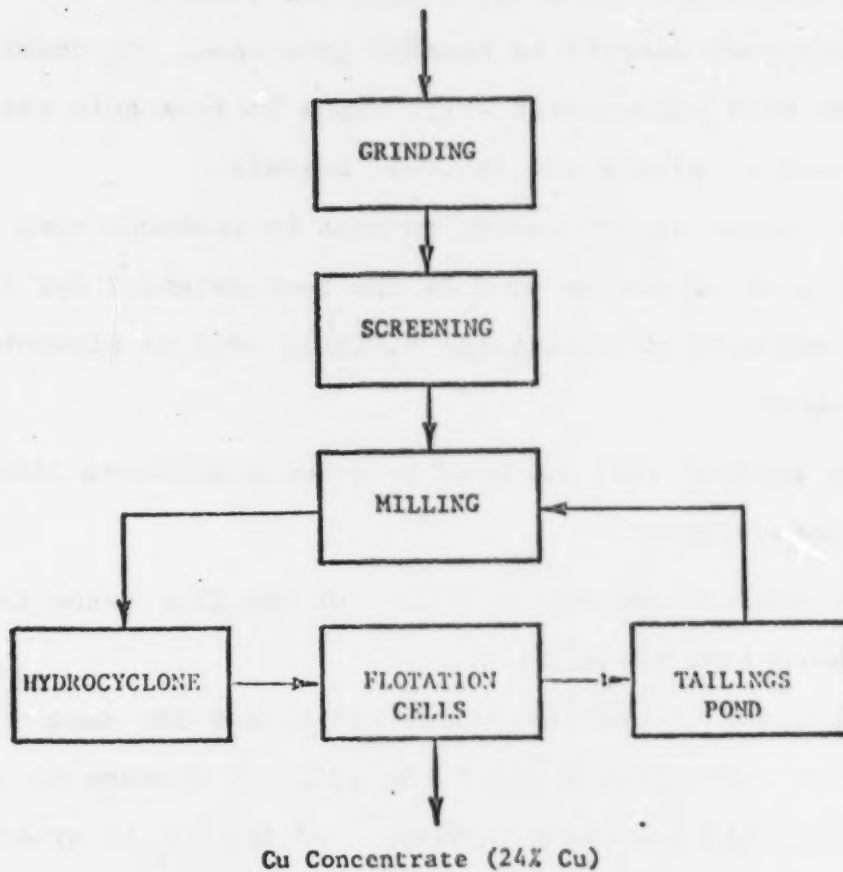


Fig. 2: Comminution and Froth Flotation [2, pg. 31]

1. To recover value-bearing particulate material which can be returned to the plant for reprocessing.
2. Environmental pollution, from the viewpoint of employees exposed to harmful gases and, SO_2 combining with atmospheric water vapor to form acid rain which damages plants and injures animals.
3. To remove value-bearing gaseous by-products such as SO_2 , which can be used as the feed material for the production of marketable sulfuric acid or elemental sulfur.
4. To recover fuel value of gaseous by-products like combustible CO.
5. To reclaim the sensible heat of the flue gases in waste heat boilers.

Optimization of smelter design can reduce the amount of environmental pollution or alter the effluent streams so that the pollutants can be easily removed. If the SO_2 is greater than 4% by volume, it can be converted into sulphuric acid without much difficulty. Typically SO_2 is converted into sulphuric acid, sulfur, or ammonium sulfate.

A survey of metals in various process streams was taken at a smelting plant owned by Radian Corporation in Austin, Texas. Table 1 is a compilation of the flow rates [7]. Some of the streams were not measured or recorded but the chart does illustrate the number of different elements present in the effluent streams.

To recover the metals from the captured particulates, it may be possible to use acid leaching and solvent extraction to selectively remove metals from low concentration leach solutions.

Electrorefining

Electrorefining is the final step of purifying blister copper to 99.99% Cu which can be used for most industrial applications. The spent electrolyte is recycled but some of the acid must be treated to remove excess nickel and unclaimed copper as well as other trace metals. Slime develops from particulates and precipitates and must be treated to recover copper and/or precious metals. Figure 3 is a flow chart illustrating the representative steps of the Electrorefining process [4]:

Table 2 lists the concentration ranges of several priority pollutants contained in the designated process streams. Slime is either discarded or undergoes further treatment for recovery of trace metals. A bleed from the electrolyte, water used to wash the anodes during preparation, and slime are the primary sources of water contamination from the electrorefining process.

Table 3 summarizes the pollutants and suggested control strategy for copper production by pyrometallurgical processes.

Table 1: Flow Rates of Metals in Process Streams

Flow Rate lb./hr.					
Element	Feed	Matte	Slag	Flue Outlet	ESP Catch
Al	400	17	700	.10	1.1
As	190	48	48	.76	30
Ba	31	33	43	.64	.023
Be	.072	4.1×10^{-3}	.032	.0034	.0004
Ca	770	12	1900	.011	2.1
Cd	59	37	.33	.076	.74
Cr	.076	.64	3.8	.044	.018
Cu	16000	18000	220	1.8	62
F	3.4	.012	2.2	9.4	.032
Fe	10000	11000	12000	.55	42.6
Hg	.018	.020	.0091	.033	.00015
Mo	79	8.5	89	.17	6.6
Ni	.70	2.0	.76	.011	.059
Pb	49	84	13	.38	5.3
Sb	6.0	4.6	3.4	.030	1.3
Se	10.	.17	5.5	.65	.16
Si	1100	42	4800	1.7	1.7
V	.92	.33	.86	.027	.011
Zn	42	31	30	.22	4.6

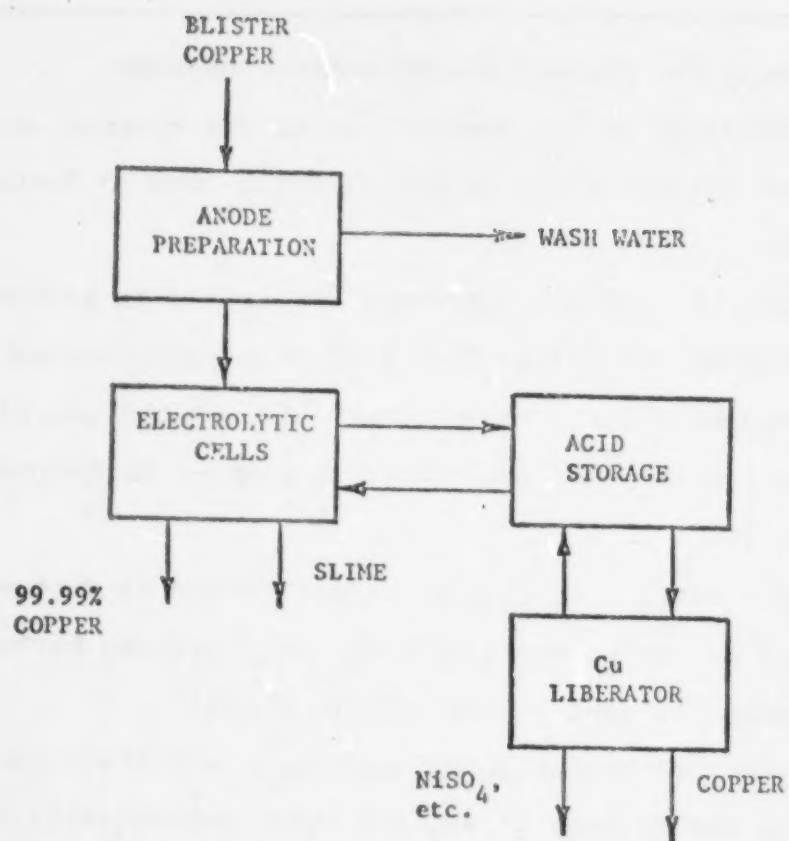


Fig. 3: Flow Chart for Electrorefining Process [4].

Table 2 : Concentration Ranges in Effluent Streams
from Electrorefining Process [4]

POLLUTANT	ELECTROLYTE (g/L)	SLIME(%)
Antimony	0.2 to 0.7	0.5 to 5.0
Arsenic	0.5 to 12.0	0.5 to 4.0
Copper	45.0 to 50.0	20.0 to 40.0
Lead		2.0 to 15.0
Nickel	2.0 to 20.0	0.1 to 2.0
Selenium		1.0 to 20.0
Silver		3.4 to 27.4

Recommended Areas for Process Modifications Research

1. Optimization of the comminution of dry mineral ore is needed to reduce the amount of water used in froth flotation.
2. Studies are needed to recover value-bearing products by dissolving the metals from particulates collected in the electrostatic precipitators through the use of solvent extraction procedures to extract the desired products.
3. Solvent extraction techniques are needed to recover copper or other metals from effluent streams before the water is sent to the tailing ponds.
4. Improve smelter design is necessary to contain and eliminate the release of SO_2 and other hazardous flue gases into the atmosphere.

HYDROMETALLURGICAL PROCESSING OF COPPER

Hydrometallurgy has three advantages over the smelting and converting processes that are traditionally used for the manufacture of copper. First, leaching is a more economical method of extraction when the ore has a low concentration of copper. Second, increasing energy costs of the furnaces are making pyrometallurgy less economical. Third, it is becoming

Table 3 Pollutants and Suggested Control Strategy for Copper Production by Pyrometallurgical Processes

Process	Pollutant	Source in Process	Nature of Pollutant	Pollutant Control Strategy
Ore grinding	Particulates	Crushers, grinders, ball mills etc.	Inorganic	Electrostatic precipitator
Froth flotation	Metals, Dissolved sludge, cyanide, pH etc.	Tailings	Inorganic and organic additives	Solvent extraction, evaporation, tailings pond
Smelting (a) Reverber (b) Electric (c) Flash (d) Blast	SO ₂ , slag and particulates	Flue gases, slag dump	Inorganic and Gaseous SO ₂	Acid plant for SO ₂ , ESP, solvent extraction
Converting	SO ₂ , slag and particulates	Flue gases, slag dump	Inorganic and gaseous SO ₂	Acid plant, ESP, solvent extraction
Anode preparation	Dissolved metals, H ₂ SO ₄	Anode wash	Inorganic	Solvent extraction
Electrorefining	Dissolved metal, H ₂ SO ₄	Electrolyte, cathode cooling etc.	Inorganic	Solvent extraction

more difficult for smelters to meet stringent environmental regulations [3].

The hydrometallurgical process entails three major steps of leaching, cementation (or solvent extraction), and electro-winning. This method of extracting copper from mineral ore has not been extensively applied to sulfide ores which are not readily leached. Because of the environmental problems associated with SO_2 , hydrometallurgy is becoming a more acceptable method of producing copper [2].

Leaching

There are numerous methods of leaching and several types of leaching solutions. Sulfuric acid is commonly used as a leaching medium, but new technology has introduced other forms of leaching solutions such as ammoniacal and ferric chloride solutions. Leaching of sulfide ores can be improved by bacterial enhancement as well. The pregnant leach solution can undergo either solvent extraction, ion exchange or cementation to recover the copper while leaving the remaining trace metals in the leach solution [8].

There are four methods of leaching [9]:

1. In situ leaching
2. Dump and heap leaching
3. Vat leaching
4. Agitated leaching

In situ and dump leaching are long term processes which can leach the ore with acid solution for several years. Because of the long period of exposure, significant quantities of the sulfide minerals will dissolve into the leach solution.

Contamination of ground water may occur and could have serious effects to the surrounding environment.

Vat leaching and agitated leaching are done with much smaller volumes of crushed ore at a much shorter period of exposure. These short term processes are useful for ores containing copper in the oxide form which dissolve easily in acid solutions. The pregnant leach solution is taken to the refining process, while the remaining sludge is either dumped or recycled for additional processing to recover other metals that were not extracted.

If the leach solution has a high concentration of copper (40 to 60 g/L) it can be sent directly to the electrowinning circuit [10]. When the solution has a low concentration making direct electrowinning uneconomical, then a process step must be taken to separate the copper from the rest of the leach solution and redissolve the copper at a higher concentration into an electrolyte. Three ways commercially available that accomplishes this task are cementation, solvent extraction, and ion exchange.

Cementation

Cementation is a reaction where copper precipitates directly onto the surface of the scrap iron. The effluents contain very large quantities of iron salts and are generally sent to the tailings pond for waste treatment.

Solvent Extraction

Solvent extraction is a process having several circulation loops where copper ions are selectively extracted from a leach solution by a specific solvent. The extracted copper

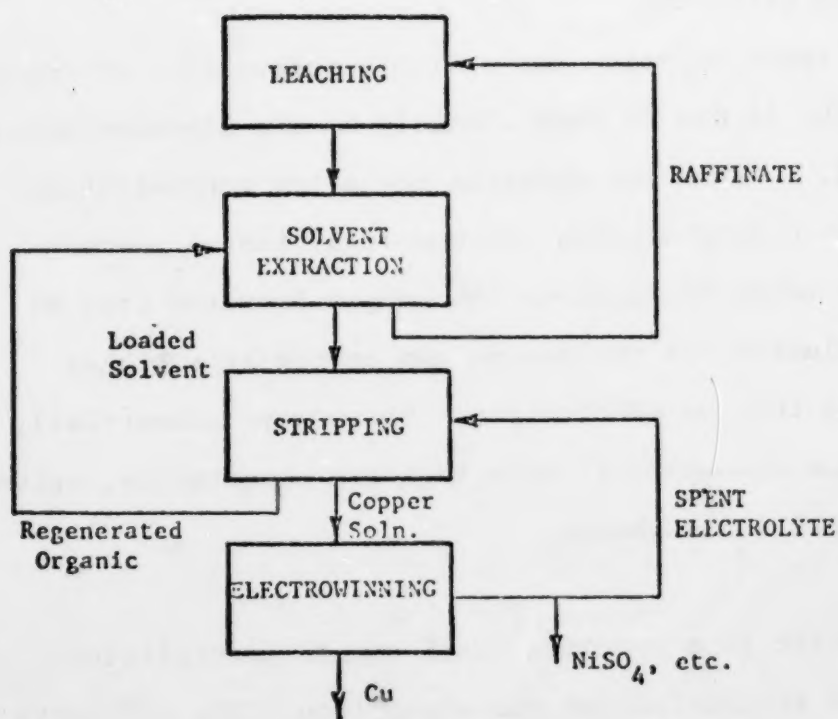


Figure 4: Flow chart of Solvent Extraction process.
[6].

is stripped from the solvent which is then recirculated into the extraction circuit. A flow chart, Figure 4 illustrates the multiple circuits of the solvent extraction process.

Some of the pollution problems that exist in this process are the build up of trace metals in the leach solution and entrained solvent in the extraction and stripping sections. Problems associated with entrainment are complicated by the unavoidable degradation of the solvent. This reduces the extraction activity of the organic material and some make up must be added to the recycle.

Table 4 summarizes the pollutants and suggested control strategy for copper production by hydrometallurgical processes.

Recommended Areas of Process Modification Research

1. Methods to recover trace metals in the effluent streams by using solvent extraction are needed. Research studies on the simultaneous extraction of several metals that are considered hazardous pollutants are needed.
2. Methods to recover the entrained solvents by filtration, flotation, centrifugal separation, etc. are needed. Study on the various methods of separating liquid-liquid mixtures would be valuable.
3. Solvents tend to degrade due to temperature, pH, or radiation extremes. The analysis of the by-products of this degradation and an effort to determine the best way to eliminate these by-products either in the recycle stream of the exit stream are needed.

4. The evaluation of new techniques for leaching sulphide ores or the development of new techniques to improve selectivity in leaching mineral ores is needed.

Table 4 Pollutants and Suggested Control Strategy for
Copper Production by Hydrometallurgical Processes

Process	Pollutant	Source in Process	Nature of Pollutant	Pollutant Control Strategy
Leaching in situ, heap, vat, agitated	Dissolved metal salts, sulfuric acid-organic additives (wet-ting agents)	Leach solution	Inorganic, metals and acid	Recycle leach solution after solvent extraction of excess metals, watch for seepage of metals into the ground water
Cementation	Dissolved metal salts	Iron ion from scrap iron	Inorganic	Solvent extraction of effluents
Solvent extraction	Dissolved metals, entrained solvents	Excess from process streams, solvent degradation	Inorganic metals and organic solvents	Improve mixer-settlers, study methods for regeneration of solvents
Electro-winning	Dissolved metals, acid, cyanide	Excess from process streams, cathode wash and cooling	Inorganic metals and acid	Solvent extraction of effluents

COAL LIQUEFACTION PROCESSES

The unpredictability of the international energy market and the very great danger of global oil shortages in the next few decades has necessitated a rapid expansion in the domestic energy base in the U.S. Consequently, the commercial production of synthetic fuels from the abundant reserves of coal is a major objective of the nation's energy research and development programs. Coal liquefaction and coal gasification technologies have received renewed interest in this regard. Economic viability and environmental impact will be the limiting factors in the commercialization of such processes.

All coal liquefaction processes produce liquids from coal by yielding a material having higher hydrogen content than coal. Fuel oils contain about 9% hydrogen and gasoline about 14% as compared to roughly 5% hydrogen in raw coal. Currently, some twenty-odd liquefaction processes are in various stages of development by industry and federal agencies. Coal liquefaction technologies can be categorized under hydrogenation, pyrolysis and hydrocarbonization, and catalytic synthesis. Of these, hydrogenation is the most advanced [11].

For this report, environmental problems associated with the Solvent Refined Coal (SRC) liquifaction technology will be discussed.

Solvent Refined Coal (SRC) Liquefaction

A fully integrated SRC liquefaction system flow scheme [12] is shown in Fig. 5. Raw coal from coal storage facilities is sent to the coal pretreatment operation where it is sized, dried and mixed with reactor product slurry recycled from the gas separation processes. The resulting feed slurry is combined with recycled hydrogen from the hydrogen/hydrocarbon recovery process and makeup hydrogen. This hydrogen-rich slurry is pumped through a preheater to the liquefaction reactor, or dissolver. Exothermic hydrogenation reactions initiated in the preheater continue in the dissolver which typically operates between 435° - 470°C. The reactor product slurry is sent to gas separation processes where gaseous products are removed. Auxiliary processes separate these gases including recycled hydrogen, SNG, LNG and sulfur species. The sulfur species are further converted to by-product elemental sulfur. Part of the separated slurry from gas separation is recycled to the coal pretreatment operation. The remainder of the slurry is sent to the fractionator. The fractionator generates three streams: a light distillate which is hydrotreated to form naphtha and fuel oil products; liquid SRC, the primary product; and a bottom stream which is sent to solids/liquids separation processes. The

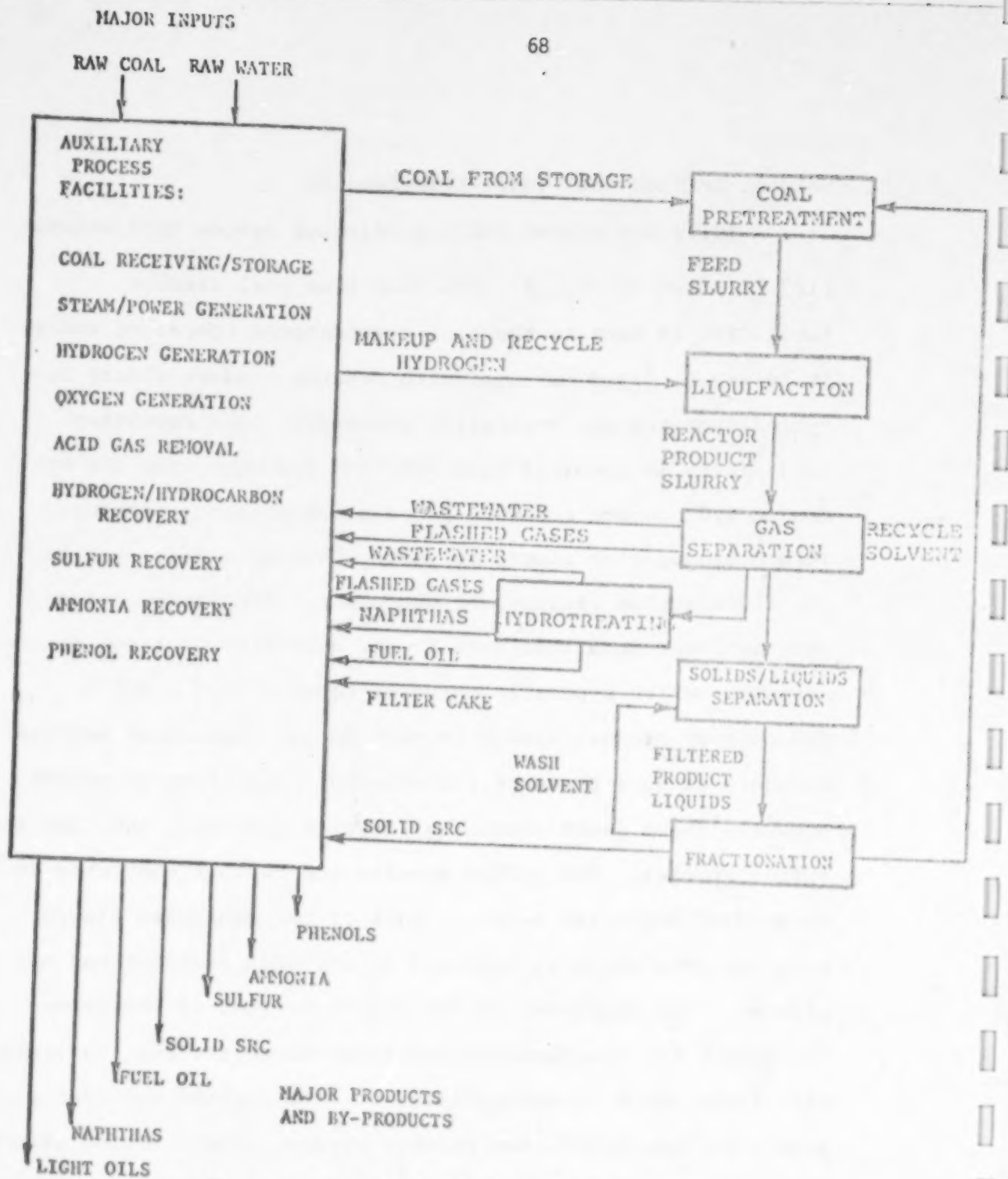


Fig. 5. Flow Sheet for An Integrated Liquefaction Process



vacuum distillation unit in solids/liquids separation recovers additional SRC liquid product from the fractionator bottoms, yielding a residue of high mineral matter content. Part of this residue is gasified to produce makeup hydrogen.

Particulate Emissions

Fugitive emissions (i.e., particulates) will be emitted from the following sources: coal storage piles, coal reclaiming and crushing, coal receiving, dryer stack gas, and ash from steam generation. Trace elements of fugitive emissions from coal preparation have a potential health hazard consisting predominantly of [13] aluminium, chromium and nickel. Trace element concentrations in particulates escaping from treated stack gas are enriched in zinc, copper, zirconium, molybdenum and selenium. The trace element concentration of coal dusts is expected to be similar to that of the parent coal, although certain trace elements may concentrate in the smaller size range. Dust (typically 1 to 100 μ in size) generated from coal receiving, storage, reclaiming and crushing is estimated to be about 24 tons/day for a 20,000 ton/day SRC II plant [14]. Table 5 lists analysis of some trace elements in dust from coal preparation after treatment with wet scrubber [13].

Suggested control alternatives for coal dust include polymer spraying, enclosed storage and water spraying. Of these, enclosed storage involves \$6 - 8 million capital investment for a 10,000 ton coal pile [14]. Cyclone and baghouse filters are probably the most effective. Due to the

Table 5 Approximate Trace Element Analysis of Coal Pre-treatment Dust after Wet Scrubbing

Element	g/day	Degree of health hazard*
Aluminum	8,910	2.21
Arsenic	3.9	2.50
Chromium	13.0	17.0
Nickel	15.0	1.3

*Degree of health hazard = $\frac{\text{concentration}}{\text{MATE value}}$

small particle range, magnetic and electrostatic filters will be needed.

Coal Pile Drainage

Coal pile runoff resulting from rainfall and such, may contain oxidation products of metallic sulfides. It is acidic with relatively high concentrations of suspended and dissolved solids [14]. The elements in this runoff include calcium, iron, aluminum and manganese. Wastewater generated in coal preparation is routed to a thickener where particulates are removed as underflow. This underflow contains about 35% suspended solids, these solids are expected to have the same elements as that in the original coal. Thickener underflow is mixed with coal pile runoff and sent to tailings pond.

Gasifier Slag and Fly Ash

One of the large volume solids to be disposed of in the

SRC plant is the gasifier slag and quenched fly ash. Current design specifications for the treatment of slag require that it be crushed, slurried with water and de-ashed. The fly ash from the quencher will be flashed down, neutralized with lime and thickened [13]. It is anticipated that this waste will be disposed of in a strip mine. The leachability of this waste is one area which needs investigation.

Residue from Solids/Liquid Separation

Solid residue from solids/liquid fractionator bottoms cannot be completely utilized in hydrogen production due to its high ash content ($\approx 64\%$). Efforts to dissolve the solid in dilute acid did not produce any leachate. Table 6 gives composition of some of the elements in this mineral residue [13] which totals about 3,700 Mg/day for a SRC-II liquefaction plant producing 10,000 ton/day liquids.

Table 6 Estimated Trace Elements Composition of the SRC Liquefaction Residue

Element	Concentration ppm
Arsenic	24.9
Barium	579
Calcium	33,323
Iron	116,760
Lutrium	2,050
Nickel	126
Sodium	1,155
Zinc	1,938

The extraction of metals from this residue is another area that requires further research.

Spent Catalyst

Catalyst used in the shift reaction in hydrogen generation has been estimated at about 135 M^3 [13]. Trace elements, sulfur compounds and heavy hydrocarbons may be adsorbed on the catalyst. The estimated life time of cobalt molybdate catalyst is three years. Regeneration of spent catalyst may not be possible due to the presence of trace metals and sulfur as well as possible sintering of the catalyst. It is suggested that valuable metals be extracted from the spent catalyst at an off-site facility. Similar facilities may be needed for spent sulfur guard and methanation catalysts.

Tail Gas From Acid Gas Removal

Acid gas from the gas purification module and gas from hydrogen production are routed to the Stretford Unit where H_2S (472 Mg/day) [13] is recovered as elemental sulfur. The Stretford process has >99.5% efficiency in sulfur recovery and can reduce H_2S concentrations to < 10 ppm. However tail gas treatment may be needed before the spent gas can be vented. The Stretford solution consists of mainly sodium metavanadate sodium anthraquinone disulfonate (ADA), sodium carbonate and sodium bicarbonate in water. The Stretford solution purge stream has a total salt concentration of 20-25%. Using a high temperature hydrolysis technique vanadium (as solid) and sodium carbonate, sulfate and sulfite can be recovered as solids. HCN is completely converted to CO_2 , H_2O and N_2 [14].

The Stretford tail gas contains about 42.7% CO_2 and 5,500 ppm hydrocarbons (as C_2H_6). Direct flame incineration and carbon adsorption with incineration (AdSox) are recommended tail gas treatment for hydrocarbons. A further scrubber might be needed to remove CO_2 in the tail gas. It is suggested that the Stretford solution be modified to reduce CO_2 emissions in the tail gas. This is one area which necessitates further research on absorption phenomena of SO_x and CO_2 in various solvents.

NO_x Removal

The reported sources of NO_x emissions within the SRC plant include [13]:

Steam generation	8.4 Mg/day
Stretford effluent gas	0.005 Mg/day

The reduction in NO_x emissions during steam generation from reducing air flow rates may not be as effective or damage-proof as other modification techniques. By supplying substoichiometric quantities of primary air to burners 40% to 50% reduction in NO_x emissions have been observed. Another useful method of reducing NO_x is by recirculation of coal flue gas [14] which lowers peak flame temperature.

Table 7 is a summary of some of the pollution problems associated with SRC liquefaction and suggested control alternatives.

Table 7 Pollutants and Control Options in SRC Liquefaction Process

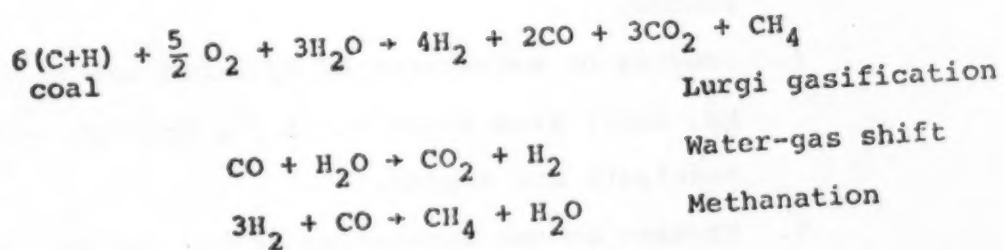
Process	Pollutants	Sources in Process	Nature of Pollutants	Pollutant Control Strategy
Coal Pretreatment	Coal dust	Storage, handling Sizing	Similar original coal	Cyclone, wet scrubbing, polymer coating, electrostatic and magnetic filters
Coal Pretreatment	Thickener underflow	Coal pile run off	Minerals and suspended solids	Extraction and disposal of tailings.
Gasifier	Slag, fly ash	--	Inorganics, metals and organics	Leaching of metals and strip mining.
Solids/Liquids Separation	Mineral Residue	Fractionator bottoms	Inorganics, metals and organics	Extraction of (toxic) metals
Hydrogen generation	Spent catalyst	Reactor	--	Extraction of Co, Mo, Ni
Acid gas removal	Tail gas	Stretford Process	Hydrocarbons and CO ₂ (=43%)	Direct flame incineration, Modification of Stretford process to remove CO ₂
Steam generation	NO _x emissions	--	NO _x gases	Substoichiometric supply of air, recirculation of flue gas

Recommended Areas for Pollution Control Research SRC-Coal Liquefaction Process

1. The applicability of electrostatic and magnetic filters to control emissions of coal dust particles in the submicron range should be explored.
2. Leachability of gasifier slag and fly ash should be estimated to determine treatment and/or disposal methods.
3. Studies on extraction of possibly toxic and/or valuable metals from solids/liquids separation residue are needed.
4. Studies on extraction of valuable metals (Ni, Co, Mo, etc.) from spent shift and hydrogen generation catalysts are needed.
5. Studies on the absorption of SO_x and CO_2 in Stretford process should lead to process modification to reduce CO_2 emissions in tail gas.
6. Modification of steam generation operation to reduce NO_x emissions is needed.

COAL GASIFICATION

For this study the pollution problems and control alternatives for the Lurgi coal gasification process are discussed. The conversion of coal to SNG involves the reaction of coal with steam and oxygen in a gasifier with subsequent gas processing to (a) adjust the $H_2:CO$ ratio by water-gas shift reaction, (b) remove acidic components, and (c) catalytic methanation. The corresponding chemical reactions are:



The four major processes in the Lurgi gasification are discussed below. A flow sheet of the process is given in Fig. 6.

Coal Preparation

Coal pretreatment in the Lurgi Systems generally consists of only crushing and screening to produce 3-35 mm particles. This larger size range compared to certain other gasification processes decreases fugitive emissions.

Coal Gasification

The coal gasifier is operated at a pressure of about 25 to 35 atm and receives coal through a feed hopper at the top and discharges ash through the bottom. Oxygen and steam

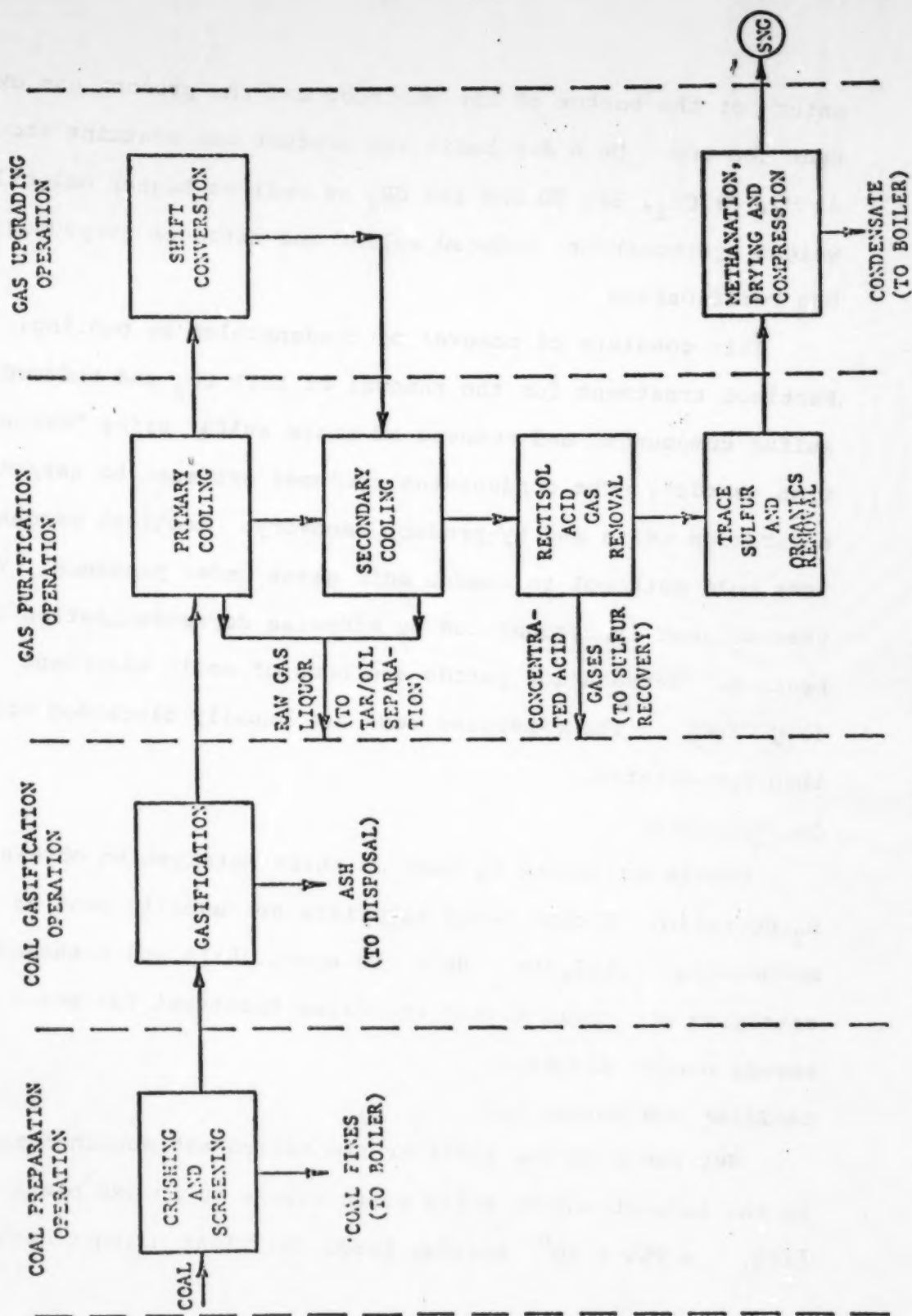


Fig. 6. Lurgi SNG Process

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enter at the bottom of the gasifier and the product gas exits near the top. On a dry basis the product gas contains about 41% H_2 , 31% CO_2 , 18% CO and 10% CH_4 as well as higher molecular weight hydrocarbons, reduced sulfur and nitrogen compounds.

Gas Purification

This consists of removal of condensables by cooling, Rectisol treatment for the removal of bulk CO_2 and reduced sulfur compounds, and removal of trace sulfur using "methanation guards". The condensates produced are sent to tar/oil separation units and by-product recovery. Rectisol process uses cold methanol to absorb acid gases under pressure. This used solvent is regenerated by stepwise depressurization and heating. Methanation guards are beds of solid adsorbent (e.g. ZnO). The exhausted beds are usually discarded rather than regenerated.

Gas Upgrading

Cobalt molybdate is used as shift catalyst to obtain 3:1 H_2 : CO ratio. Nickel based materials are usually used as methanation catalysts. Both the spent shift and methanation catalysts are solid wastes requiring treatment for metal recovery and/or disposal.

Gasifier and Boiler Ash

Net ash from the gasifier and boiler ash quench systems is the largest volume solid waste stream in an SNG plant [15]. A 250×10^6 Scf/day Lurgi SNG plant using a coal

containing 15% ash is expected to generate about 5400 ton/day wet ash having = 2% moisture content. It contains leachable inorganic and organic materials. These constituents can be possible sources of groundwater contamination. An alternative disposal scheme would involve stabilization to convert the wastes into a chemical form that is more resistant to leaching in the ultimate disposal site. Table 8 presents typical leaching study results for wastes stabilized by Chemfix process [16].

Table 8 Laboratory Leaching Results of Chem-Fixed Refinery Wastes

Element	Concn. in Raw Sludge ppm	Concn. in approx. 200 ml Lecheate water after Chem Fix ppm
Total Chromium	43.5	< 0.1
Iron	1310	< 0.1
Zinc	88.0	< 0.1
Nickel	8.9	< 0.1

The leachability of ash produced in Lurgi SNG is an area which required further investigation.

Spent Guard Catalyst

Zinc oxide beds are used for removing the last traces of sulfur after and gas removal has removed all but a few parts per million. Water vapor content is critical in that liquid water can possibly degrade ZnO bed completely [17]. The sulfur loading capacity of ZnO catalyst increases from =5 wt%

at 273°K to $\approx$ 20 wt% at 673°K. However maximum recommended loading is only 3 wt% when the desired exit gas specification is 0.02 ppm H_2S [18]. Spent methanation guard material will consist primarily of zinc sulfide and unreacted zinc oxide. Operating data on the quantity and composition of spent methanation guard catalyst are needed [15] to evaluate the disposal and/or reclamation of the spent catalyst.

Spent Shift/Methanation Catalysts

Catalysts used for shift and methanation require periodic replacement; the spent catalysts constitute a solid waste. Gross composition of spent catalyst is not expected to be dramatically different from that of fresh catalyst, although accumulation of carbon, sulfur, and metallic elements is to be expected. Data is needed on the characteristics of spent Lurgi SNG catalysts. Cobalt-Molybdate is used as shift catalyst. Table 9 presents pilot plant data on spent Harshaw Ni-0104-T-1/4 catalyst [19].

Table 9 Spent Harshaw Nickel Catalyst Analysis

	Typical Fresh Catalyst	Bottom of first stage methanation	Top of second stage methanator
Sulfur, % wt.	0.15	3.7	0.16
Carbon, %	3.4	3.4	4.5
Nickel, %	60.0	52.0	61.0

Spent nickel methanation catalyst is as active as zinc for trace sulfur removal and can be used as sulfur guard catalyst [17]. Sequential interchange of the first and second stage

methanators is also recommended, as it is apparent from Table 9 that the catalyst at the top of second stage methanator is almost fresh. In the end however spent methanation catalyst constitutes a solid waste. The large wt. % Ni on the catalyst would be an economic incentive for reclaiming metal from spent catalyst. Data on the properties of spent nickel methanation catalysts and the applicability of metal extraction for reclamation are two areas that need further investigation. Further, the spent catalysts although of small quantity are of special concern due to their content of potentially toxic metals (Ni, Co, Mo) and coal-derived organics (metal carbonyls for example) and trace elements. Fixed-bed methanation/shift reactor system is reported to have the advantages of (i) operation at conditions removed from carbon formation, thereby increasing catalyst life, (ii) reduction in catalyst sensitivity to sulfur, and (iii) need CO_2 removal from a reduced volume of gas. However, this has not been commercially demonstrated yet [17].

Ash Quench Slurry

An ash quench slurry results when process waters are used to cool and transport gasifier ash to a settling unit or disposal site. No operating data are available for ash quench slurry characteristics [15]. Laboratory data indicates that this slurry can contain up to 20 g/L of dissolved solids with the dominant ions being [20] Ca^{++} , SO_4^{--} , K^+ and Na^+ . An increase in the solubility of Fe, Mn, Cd and Al is also expected with decreasing pH. In addition, the concentration of certain hazardous elements (e.g. As, Ni, Cr and Cu) can

reach levels which warrant control of the ash slurry discharge. Characterization of ash slurry water is needed to evaluate pollution control alternatives such as coagulation and flocculation of solubles.

Phenol Recovery

Gas liquor from tar-oil recovery contains a high concentration of phenols, up to 4200 mg/L [15]. The Phenosolvan process using Butyl acetate as solvent is used to extract these phenols. Most of the available data on the performance of this solvent extraction process are for the unit in Sasolburg, South Africa. Solvents suggested for Phenosolvan process include butyl acetate, isopropyl ether and light aromatic oil [21,22]. For butyl acetate the distribution coefficients in Table 10 for various phenolic compounds have been reported [22].

Table 10 Distribution coefficients for various phenols in Butyl Acetate at 300°K

Compound	K_D^*
Phenol	65
3,5 xylenol	540
Pyrocatechol	13
Resorcinol	10

$$*K_D = \frac{\text{wt. fraction in solvent phase}}{\text{wt. fraction in aq. phase}}, \text{ measured at high dilution}$$

The solvents can remove only limited amounts of non-phenolic organics. A better characterization of the available solvents for phenol extraction and their removal efficiencies for various phenols are needed. Further development of solvent extraction systems to remove nonphenolic organics is also

suggested.

Removal of Sulfur Compounds from Rectisol Process

In terms of total volume and content of H_2S and other reduced sulfur compounds, concentrated acid gas from the Rectisol process is the most important gaseous waste stream in a Lurgi SNG facility. Some of the control options for concentrated acid gas stream [15] are shown in Table 11.

Table 11 Control Options for the Concentrated Acid Gas Stream

Control Options	Comments
1. Claus Plant Sulfur Recovery	High concn. of H_2S in tail gas; feed gas H_2S enrichment and Hydrocarbon removal are needed
2. Claus Plant Sulfur Recovery and tail gas treatment	Not highly effective at high levels of CO_2 in feed, applicable only for streams containing 5-15% H_2S
3. Claus Plant Sulfur recovery and SO_2 control/recovery	Reasonable option when feed gases contain more than 5-15% H_2S
4. Stretford Sulfur Recovery	Inapplicable to waste gases containing greater than 15% H_2S ; not economical at high CO_2 levels; discharge may contain high COS and HC levels

The determination of best option for the management of a specific sulfur bearing gas stream must be made on a case by case basis due to the restrictions on feed compositions and economics for different processes. Some of the above options have not appeared in commercial design [15] due to the lack of engineering data. It is suggested that research

be organized to provide operation data for various sulfur recovery, SO_2 and tail gas treatment processes.

Table 12 summarizes some of the pollution problems associated with the Lurgi SNG process and suggested control alternatives.

Recommended Areas for Pollution Control Research—Lurgi Coal Gasification Process

1. Stabilization of gasifier and boiler ash is needed to decrease or prevent leachability.
2. Operating data and composition on spent methanation guard, shift and methanation catalysts is needed to determine possible extraction of valuable and toxic metals.
3. Studies on the use of spent methanation catalyst as sulfur guard would be valuable.
4. Development of solvent extraction systems is needed to remove nonphenolic organics and determination of distribution coefficients for existing solvents.
5. Engineering data on various sulfur recovery, SO_2 and tail gas pretreatment processes is needed.

CONCLUSIONS AND RECOMMENDATIONS

The results of the process analysis presented above and further studies conducted [1] indicate that a number of fruitful research programs of a broad enough scope can yield results which would apply to solution of toxicant problems through process modification. These programs are delineated below.

Table 12 Pollutants and Control Options in Lurgi SNG Process

Process	Pollutants	Sources in process	Nature of pollutant	Pollutant control Strategy
Coal Gasification	ash	--	leachable inorganic, organic materials	stabilization of ash to decrease or prevent leachability
Gas Upgrading	Spent methanation guard catalyst	Methanation guard reactor	ZnO with trace organics, sulfur and metals	Reclamation by extraction
Shift/Methanation	Spent catalysts	Reactors	Co, Mo, Ni, with trace organics, sulfur	Spent methanation catalyst as methanation guard, extraction of toxic metals from spent catalyst
Coal Gasification	Ash quench slurry	Thickener overflow	Dissolved inorganics, hazardous metals (As, Ni)	Coagulation and flocculation to remove dissolved salts
Tar/oil separation	Phenols in gas liquor	--	Nonphenolic organics	Better characterization of solvents to modify/develop extraction systems
Acid gas removal	Sulfur compounds	Rectisol tail gas	SO ₂ , H ₂ S, CO ₂	Clans sulfur recovery and SO ₂ tail gas treatment, Stretford sulfur recovery

Solvent Extraction

Modification of solvent extractor design and operation would minimize metal ions or non-phenolic organics in process streams leaving extractor batteries in hydrometallurgical and coal liquefaction processes respectively. Studies could include modelling of selective ion extraction in multiple metal systems, characterization of liquid dispersion properties such as surface area and droplet mixing as a function of power consumption, extraction kinetics, and separation of liquid-liquid dispersions.

Catalyst Deactivation

Modification of catalyst reactor bed operation and studies on catalyst deactivation will increase catalyst life and reduce the volume of spent catalyst from coal gasification operations. Studies could include modelling catalyst deactivation phenomena as affected by temperature, pressure, feed gas composition, catalyst structure, and catalyst type. Optimal reactor operation studies for sulfur guard catalysts (ZnO), shift catalysts (cobalt-molybdate), and methanation catalysts (nickel) can be conducted.

Leaching Processes

Modification and improvement of leaching processes for sulfide or oxide ores will reduce ground water contamination and dissolved metal salts in process streams in hydrometallurgical processes. These results also apply to recovery of metals from particulates (smelting dust), coal liquefaction ash, spent catalysts in coal gasification, and coal liquefaction residues. Studies could include vat leaching using ammoniacal or inorganic

acid solutions. Characterization of kinetics of leaching as affected by particle size, temperature, concentrations and particle structure can be explored. Minimum power requirements to suspend particles and maximize particle-liquid mass transfer can be studied.

Gas Absorption

Modification and improvement of gas absorption processes such as the Stretford absorption process will reduce emission of H_2S , HCN , and CO_2 in tail gases from coal liquefaction processes and H_2S and SO_2 for smelter off gas recovery operations. Studies could include gas-liquid mass transfer and gas-liquid reactions in absorption liquids (sodium meta vanadate, sodium carbonate, sodium bicarbonate, and ADA) as affected by temperature, pressure, and gas-liquid contacting.

Gas-Liquid-Solid Reactions

Modification and improvement of reactors for contacting and reacting gas-liquid-solid dispersions would minimize particulate emissions in coal liquefaction reactions as well as vat leaching processes. Studies could include coal dissolution rates, gas dispersion, particulate agglomeration, dissolved gas-particle reactions, and determination of the rate limiting steps as affected by mechanical agitation, temperature, pressure and compositions.

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TOXICANT WORKSHOP

CHICAGO, ILLINOIS

June 15, 1982

TOXICANT ELIMINATION BY EDICT AND DESIGN

George Herr

Eli Lilly and Company

TOXICANT ELIMINATION BY EDICT AND DESIGN

Good afternoon. It is good to be here although, in all truth, I'd much rather be eluding frustration on a golf course. I come with no great revelations or magic methods to forever eliminate toxic chemicals from your plant effluent.

This is the story, not of some great change in the design of a process to eliminate or neutralize a toxic chemical and thereby prevent its entry into the environment but, instead, it is the story of a bold new concept adopted at considerable risk and brought into reality by the courage and dedication of many people across a whole plant site and throughout a company. It goes to prove that there is some truth in the saying, "Where there's a will, there is a way."

In the late 1960's Eli Lilly and Company found the need to construct additional manufacturing capacity to make large quantities of two new products. Early in the pre-engineering planning stage, it was decided that the plant would operate in harmony with the environment. All engineering design was carried out with that underlying goal in mind. A policy was adopted which dictated that conventional means of treating wastes would be used only as a last resort and that new and innovative methods of treatment would be researched and installed. Our process people were given the challenge of designing manufacturing processes to produce a minimum of waste and to provide a maximum degree of harmony with the environment. It must be said that we lucked out. The processes to be run at our Clinton plant responded to this strategy very well.

Early in the planning stage, a permanent cadre of people was named; and they, in effect, were isolated from the rest of the company. They were told to forget about conventional waste treatment methods and to develop new ones. Contact between this cadre and the rest of the company was frowned upon. They were to remain purists and were not to be contaminated by any nonchosen people or by any existing knowledge of conventional process methods.

This approach was a radical one to say the least. It also caused quite a bit of comment and head scratching both within and outside the planning group. As "an outsider," I at first questioned the wisdom of the approach being used. My feelings were hurt. Ten years later as I view a very successful operation, I have to swallow my pride and admit that they did it without me.

Soon after this ambitious approach was adopted and before any active planning began, several fundamental concrete goals were set. They were:

1. No waste of any kind would leave the site.
2. No organic wastes would be buried on or off the plant site.
3. Effluent discharge to the river would not raise the river temperature by a significant amount.
4. Water conservation would be practiced by maximizing the recycling of water.
5. Solvents and raw materials would be recovered and reused wherever possible.
6. Microbiological waste treatment would be avoided.

These goals were easy to set but much harder to meet.

In any manufacturing plant, raw materials that enter the plant meet with one of three ultimate fates:

1. They can be processed successfully into desired product.
2. They can be recovered and recycled.
3. They can be treated or destroyed and the residuals sent to the river or the atmosphere or off-site.

In this plant, about 80 percent of all the materials entering the plant wind up as waste and must be disposed of in some manner. This fact made the goals stated above difficult to achieve.

In the quest for new technology to be used to destroy or treat wastes, many methods were investigated on paper, at bench scale, and in pilot scale. These methods included:

Chemical oxidation

Physical chemical combination

Carbon adsorption

Hydrolysis

Submerged combustion with stripping

Ultra filtration

Evaporation

Recompression

Falling film

Oil addition

Incineration

Fluid bed

Multiple hearth

Rotating kiln

Thermal oxidation

Traveling grate

To make our task even more challenging, the Clinton plant was built on a "fast-track" schedule. New methods had to be discovered, devised, created, or what have you on a crash basis. These methods then had to be evaluated and compared with other methods. When the choice was made, the system was designed and the equipment purchased and installed all under great temporal pressures. These systems were all new; and now, ten years later, they are still being modified and fine tuned.

Because of our determination to stay away from conventional methods of waste treatment and to live in harmony with the environment, we wound up with the following array of equipment:

1. Three thermal oxidizers (No. 4 is now in construction.)
2. A four-stage evaporator made by the Carver Greenfield Company
3. A pyrolyzer made by Midland Ross
4. A rotary kiln made by Bartlett Snow
5. A package unit to treat human wastes microbiologically
6. A waste heat boiler purchased from Combustion Engineering

Some of these methods are familiar to you, and some are not. I'd like to spend a little time briefly describing each of them; the way they were selected; what they accomplish; and, in one case, recount the agony of victory in installation, shakedown, and operation.

As a general rule, the wastes from a chemical manufacturing operation are difficult to biodegrade and lend themselves much better to incineration as a disposal method. To deal with these biorefractive wastes, we elected to go with thermal oxidation. A thermal oxidizer is used to destroy waste solvents, both concentrated and dilute, as well as spent reaction mixtures that contain biorefractive starting

materials and by-products. The oxidizer consists of two combustion chambers. The primary chamber is used to destroy solvent-water mixtures containing 90+ percent solvent. In the secondary chamber, where solvent-water mixtures of less than 10 percent solvent are destroyed, the combustion heat produced in the primary chamber is used to evaporate the water contained in the secondary waste. The contained organics are then thermally destroyed. These units have forced draft fans with motors of up to 500 hp capacity. (These have to be housed to prevent noise pollution.) The feed to the oxidizers can contain halogenated compounds or compounds of sulfur; thus the combustion products can contain acidic gases which must be scrubbed out of the exhaust air stream before it enters the environment. This is done using dilute caustic. The waste stream also contains inorganic salts which appear in the exhaust air stream after scrubbing as a very fine particulate. In order to minimize the particulate load to the atmosphere, we employ high pressure drop Venturi scrubbers--about 70" of water across the Venturi and 90" across the quench and scrubber.

Carver Greenfield Pyrolysis

Since one of the products to be manufactured was to be made by a fermentation process, it seemed like heresy to treat the wastes from this process in any way other than by microbiological waste treatment.

An analysis of this process and the intended use of its product revealed that microbiological treatment for this waste would have been the wrong choice because this product which was to be used as a growth stimulant in animals was potent enough so that it had

to be diluted with something. What better diluent than something with a high nutritional content. It is a fact that the tiny cells called mycelia which produce this product, plus the unused raw material in the fermentor, have a very high nutritional quotient.

So putting all of these factors together, our process people were challenged to design a process whereby we could take the total content of the fermentor (or the whole broth which contains the growth activity, the mycelia, and the unused nutrients), evaporate the water, dry the residue, and market it as the product.

These materials, which we now sell as part of our product, contain BOD₅ equivalent to a human population of 400,000 people.

The only true wastes which arise out of this process are from spoiled fermentors (which we naturally work very hard to hold to a minimum) and fermentor washes from both good and spoiled fermentations. These washes, which contain relatively little biodegradable material, are concentrated in our Carver Greenfield evaporator. This is a four-stage evaporation system. The first three stages operate in a water matrix while the fourth stage is used to transfer the waste from the water matrix into an oil matrix where it can then be dealt with very effectively in a starved air pyrolyzer and where, in a cracking process, methane is produced. The methane gas from the pyrolyzer is burned in a waste heat boiler. The steam generated in the waste heat boiler is used back in the evaporator section. Any surplus steam is fed back into the plant system. The char from the pyrolyzer goes to an on-site landfill.

To dispose of miscellaneous wastes, domestic trash, empty combustible containers, filter papers and cakes, and innocuous but flammable process wastes, a rotary kiln incinerator was purchased from Bartlett Snow and is now being used. This is a versatile piece of equipment and handles trash not only from Clinton but also from other Lilly plants. It has a secondary combustion chamber with gas-fired after burners. Because of the particulate matter in the stack gases, they are run through a high pressure drop Venturi (about 50" of H_2O) in which the water is pH controlled with dilute caustic.

Our processes at Clinton use large quantities of organic solvents. In any process industry, it is mandatory for favorable process economics that as much solvent be recovered as is possible. At the Clinton plant, we built stripper columns that not only were economically efficient but also went far beyond the critical point of diminishing returns so that the last bit of recoverable solvent could be squeezed out and prevented from entering the environment.

In many of the systems described above, we were pioneers. We found ourselves on the frontier of "State of the Art." We were the unwitting possessors of the first or second production size unit. When we started up, not much was known about running at our scale. We developed or redeveloped many new design engineering concepts. In some instances we got far more attention from the vendor after we had debugged his equipment than before. "Before" was when we were in deep trouble and needed not only attention but also help. None of these units started up easily, and only the dogged determination of our people rendered them amenable to routine operation.

After smooth running conditions were achieved, we became the show and tell place for that particular piece of equipment--so much so that we finally had to greatly curtail many vendors' activities on our plant site.

In our plant design, we were concerned with every aspect of the environment, one of which was conservation of water as a natural resource. Our plant has almost as many cooling towers as there are grains of sand on a beach. Very few drops of water reach the Wabash River without having toured our plant several times. Our blowdown rate is about 10 percent.

In our endeavor to save water, we adopted many measures which not only conserved water but also helped us in all our waste treatment processes. In many instances it is hard to tell where these policies do the most good--in water conservation or waste treatment. Some of the methods adopted were:

1. Prohibition of barometric condensers on steam jets.
2. The elimination of floor drains in production buildings. Instead of flushing the floors with large quantities of water to clean them, the operator must use a broom, shovel, vacuum, and damp mop.
3. Water-saving, highly efficient devices are used for cleaning equipment and surroundings.
4. We use self-closing faucets wherever possible throughout the plant.
5. In some instances, dilute wastewaters can be reused as a first rinse on dirty equipment cleanup.
6. Acidic and basic waste streams are used to treat each other thus eliminating unnecessary dilution of waste streams.

One result of these water conservation measures is that less than three percent of the water that enters the plant has to be dealt with as a waste stream.

Wherever tankers or rail cars are loaded or unloaded, we have covered spill pads and sumps to collect any spills and minimize the possibility of any portion of a spill leaving the plant site. These pads and sumps are only the start of our spill prevention and countermeasure plan. They must be tended constantly and the sumps kept free of rainwater. All of this requires special equipment and manpower.

The waste conveying systems are designed, instrumented, and constantly monitored so that any accidents which result in spills are detected very soon after occurrence. These systems are set up so that sections of the plant and waste collection system may be isolated to contain spills or upsets.

It must be said that any spill automatically becomes a plant emergency and its correction becomes the first order of business. The concern for the safety of our people and neighbors is the only thing that can take priority over our immediate concern for the environment.

To give you an idea of the troubles encountered in starting up some of this new equipment and bringing it on line to operate in a reliable manner, I would like to recount the saga of the start-up of our evaporator-pyrolyzer waste heat boiler.

The original system consisted of a three-stage evaporator. The first two stages concentrated the feed stock, and the third dried it. Also included in the system were a centrifuge and a waste heat

boiler. The boiler was designed to provide 27,000 kg/hour of steam at 170 psi.

The start-up of the evaporator went smoothly, and it ran relatively trouble-free for three months; and then the honeymoon was over. The drying stage fouled and completely plugged up with a taffy-like substance. After an intensive investigation, it was found that the substance resulted from sugars that had been added to our fermentation process as nutrients.

In a relatively short period of time, other process changes were made which resulted in more trouble. We upped our use of cleaning compounds which introduced more sodium ion into the system. The sodium combined with the fatty acids in the waste mixture to produce soapy emulsions.

We found that we could solve the problem caused by the sugars by allowing them to biodegrade in storage before processing. This temporal bubble in the line amounted to only a few hours.

The fatty acid soap problem took longer to solve, but we found that if the ratio of solids to oil was properly adjusted and the use of the centrifuge eliminated, the rest of the evaporator could be operated without plugging up.

We solved the evaporator problem and then ran into trouble with the waste heat boiler. The combustion of the sodium salts of ~~fatty~~ acids generated low melting eutectics. This problem was partially solved by taking the following measures. We added:

1. A tap to the boiler floor to remove slag.
2. We added retractable soot blowers to clean boiler tubes.

3. We replaced our dust collector with a high energy wet scrubber.
4. We installed a precoat filter to remove the suspended solids from the scrubber blowdown.

These revisions were completed in mid-1972, and the boiler performed well but at a staggering price. The steam usage for soot blowing was 75 percent of what the boiler produced. The whole process became a large user of energy. In addition, every month the boiler had to be shut down for extensive tube cleaning. Ordinary boiler maintenance was excessive. Our labor requirement went up 25 percent because of the precoat filter.

Finally, everything was straightened out, and then plans were announced to expand the plant. It never fails to happen. Neither boiler nor evaporator was big enough to handle the increased waste load.

We had 12 months in which to figure out a way to handle the increased load. Facts that had to be taken into consideration were:

Since the original installation of the evaporator, the energy picture completely changed, which caused us to reconsider our decision to avoid activated sludge. However, after much experimentation, pilot, work, and pencil pushing, it was decided to add a fourth stage to the evaporator and interject a pyrolyzer between the evaporator and the waste heat boiler. The design for the evaporator-pyrolyzer-boiler process was finished in 1974 and start-up began in 1976. The process now consisted of a four-effect evaporator, a pyrolyzer, and the original boiler which had been modified.

Once again, we were first with a piece of equipment. Ours not only was the largest pyrolysis furnace of its kind, but also, it was the only one.

The pyrolyzer started up fairly easily, but it took nine months to get it to run smoothly. Between the fourth stage of the evaporator and the pyrolyzer, we had installed a centrifuge. The centrifuge removed more oil from our waste solids than had been removed from these solids during the pilot tests. While this was good for the economics of the process, it required many changes in equipment before any degree of reliability could be achieved in the operation of the pyrolyzer:

1. We installed a spreader mechanism to spread the feed on the pyrolyzer hearth.
2. We revised the hearth plow and auger mechanism to facilitate the removal of the char.
3. We converted to a wet bottom hopper to prevent post pyrolysis burning of the char.
4. We modified the gas burners and relocated them so that we would not melt the char.
5. We had to revise the water seals on the unit to prevent nuisance shutdown caused by seal failure.

When all these changes had been complete, the unit was started up again; and beyond routine maintenance, it operates fairly smoothly now. Naturally, when the vendors learned that we had debugged the process system, we got a flood of requests to show and tell.

This plant was built with a keen sense of environmental awareness. This sense is part of every person's conscious and subconscious who works on the plant site, and is something that must be reinforced every day. From the day a new hire enters the work force, his duty to perform his job in such a manner as to protect the environment is drilled into him through many special classes as well as on-the-job training. So much emphasis is placed on this aspect of his training that it becomes second nature to him. This awareness is constantly reinforced by refresher training.

The Clinton plant has been on stream for over ten years. We have not met all of our goals as yet, but our track record is good. A look at our scorecard reveals that:

1. We have successfully avoided microbiological waste treatment and its attendant problems except for the small package unit used to treat human waste.
2. We recirculate what ~~must~~ be considered a maximum amount of cooling water.
3. We have held to a minimum the volume of wastewater which must be treated.
4. We do not bury any organic wastes either on or off the site.
5. We recover for reuse solvents and raw materials wherever we can. The best example of this is the use of mycelia as a carrier for the fermentation product that it synthesizes, which greatly reduces the amount of waste we must deal with.
6. The effect of our effluent on river temperature has been minimal.
7. We had originally intended that no wastes leave the plant site. However, on occasion, some wastes are shipped to other sites for disposal. This is the one goal which has not been fully met.

Our solution to the problem of keeping toxicants out of our effluent at Clinton and, hence, out of the environment has been to design our production processes to minimize the size of our waste streams.

The waste streams are then subjected to energy intensive treatment methods which tend to destroy the toxicants. This strategy has required much long-range planning, diligent maintenance, and constant reinforcement. It has been worthwhile and very successful.

MICHIGAN'S EXPERIENCES WITH INDUSTRIAL PROCESS
CHARACTERIZATION IN NPDES PERMIT DEVELOPMENT

Gerald W. Saalfeld
Office of Toxic Materials Control
Michigan Department of Natural Resources

Introduction

I am an aquatic biologist with the Michigan Department of Natural Resources (MDNR) in the Office of Toxic Materials Control (OTMC). A primary function of our Office is to evaluate NPDES permits and pretreatment programs as to their adequacy from a toxic substances control perspective. To perform this function effectively we must be able to accurately identify and quantify toxic chemical substances in industrial/municipal effluents; and we must also be able to develop, at least, an elementary understanding of the individual process operations used by facilities applying for permits to discharge wastewater to the waters of our state. MDNR's experiences in NPDES permit development have indicated that the standard permit application package submitted by industrial dischargers does not always provide an information base which is sufficient to satisfy these critical prerequisites. MDNR recognizes that there is a definite need to develop innovative mechanisms which are capable of accurately characterizing complex and dynamic industrial effluents for toxic chemical substances in a manner considered cost-effective and acceptable by industry. Since 1980 our Office has been evaluating, with U.S. EPA - Region V assistance, the concept of industrial process characterization (IPC) as a potential solution to some of the toxics-related wastewater characterization problems currently plaguing our NPDES program.

IPC, as it has been used in Michigan, involves a comprehensive review of the process operations, raw materials used, unintentional and intentional byproducts formed, final products manufactured, and waste treatment and disposal practices of an industrial facility.

The objectives of an IPC study are to:

1. identify and quantify the constituent concentrations of toxic chemical substances which are or may be discharged to receiving waters from individual and combined process operations; and
2. provide a data base representative of individual facility process operations that can be used by MDNR staff to develop appropriate water quality-based and technology-based effluent limitations for toxic chemical substances; and monitoring requirements which are meaningful and representative.

The purpose of this presentation is to overview a study format designed by our Office for performing an IPC study at an industrial facility; to present the criteria used by MDNR to select potential candidate industries for IPC; and to briefly discuss the advantages and limitations of IPC as we perceive them based on our observations and experiences in the program to this point.

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MDNR's Industrial Process Characterization Study Format

MDNR's involvement with IPC was initiated in 1980. We soon concluded that before IPC could be realistically incorporated into our NPDES program, it would be necessary to first develop and field verify a study format which outlined the framework and detailed procedures associated with an IPC study. The IPC study format which was eventually developed and is currently being field verified by our Office consists of 5 distinct phases. A phased approach was selected so that an IPC study requirement could be fit nicely into a facility's NPDES permit. Individual dates of compliance are usually established in the permit for each phase of an IPC study.

The first phase of the IPC study format is entitled -- Submission of Background Process - Related Information. In this phase, the Company is requested to respond to a set of 19 questions (Attachment I) which are designed to provide MDNR staff with, at least, an elementary understanding of the facility's process operations, chemical usage/manufacture and waste treatment/disposal practices. The Company is not required to provide background information for process operations which have no potential of contributing water to the facility's final effluent(s). Therefore, "dry" process operations are not considered to fall within the scope of an IPC study. Chemicals that are used in laboratory quantities (less than 2 kg/month) also are not required to be reported. MDNR's request for analytical chemistry data available characterizing the composition of internal waste streams has been, as one might anticipate, a point of controversy for some industries. However, it should be noted that some industries have been very willing to share this type of information. Frequently, the preparation of complete responses to some of the Phase I questions require the submittal of process-related information considered proprietary by the Company. Therefore, it is imperative that MDNR have adequate confidential information handling procedures available which encourage effective participation by the industry.

The second phase of the IPC study format is called -- Development of Intuitive Parameter List. In this phase, Company and MDNR staff cooperatively develop a list of chemical substances which are considered to have a potential to be present in the facility's final effluent(s). They also predict the "worst case" final effluent concentration(s) for each chemical substance on the list. The list of chemical substances is referred to as the intuitive parameter list.

The third phase of the IPC study format is called -- Cooperative Development of Final Analytical List and Sampling Protocol. This phase can be very time consuming, primarily because each chemical substance on the intuitive parameter list must be hazard assessed by MDNR staff to determine whether the chemical has a potential to be discharged at or above a concentration considered to be of concern to the environment or public health. This hazard assessment process involves a comprehensive review of the toxicological data available for the chemical, in addition to, a site-specific evaluation of the chemical's exposure potential. Those chemical substances determined

to have the potential to be discharged at or above concentrations of environmental or public health concern are included on the final analytical list. When the final analytical list is complete, a sampling protocol is prepared which identifies the following information for each chemical substance on the list:

- sampling location(s)
- sample type (grab, 24-hour composite, etc.)
- sampling frequency and duration
- analytical method
- sample preservation techniques

The fourth phase of the IPC study format is called -- Quantitative Analysis. In this phase the Company is required to analytically quantify the effluent concentration(s) of each chemical substance on the final analytical list according to the procedures set forth in the sampling protocol.

In the final phase of the IPC study format -- Submission of Final Report, the Company submits to MDNR the results of the quantitative monitoring in addition to any interpretation of the data they care to provide. The final report must bear the certification of the Company that it has been objectively and professionally prepared.

MDNR uses this study format as a starting point when confronting an industry with a permit condition that requires their performance of an IPC study. We support and encourage appropriate modifications in the study format when they are necessary to account for facility-specific needs. However, format modifications which would compromise the primary objectives of an IPC study are not approved.

MDNR's Process for Selecting Candidate Industries for Industrial Process Characterization

The selection of candidate industries for IPC is a difficult and challenging task. Unfortunately, there are no firm set of rules or criteria that can be used to simplify the process. However, we believe that IPC studies provide valuable assistance in developing NPDES permits for those industrial facilities that fall into one or more of the categories identified below:

Category I

Industries discharging effluents that change significantly in chemical composition and, subsequently, can only be characterized adequately for toxic chemical substances using sophisticated sampling protocols.

Category II

Industries that submit questionable or incomplete permit applications that do not appear to accurately reflect the nature of their process operations.

Category III

Industries suspected as being a source of a known toxic chemical-related environmental contamination problem, and a traditional analysis of the facility's final effluent(s) for the chemical of concern is not capable (due to analytical capabilities or waste stream masking) of determining whether the facility is actually a contributing source of the chemical.

Category IV

Industries requesting permission to discharge wastewaters generated by new or modified process operations that cannot be characterized adequately using the permit applications or available literature.

Advantages of Industrial Process Characterization

IPC offers several benefits to the NPDES programs of State/Federal regulatory agencies which deserve mention here.

- One of the major benefits of IPC is that it allows for the development of sophisticated sampling protocols. This capability ensures that chemical substances are sampled when they have the greatest potential of being present in a waste stream or effluent.
- A second benefit associated with IPC is that analytical resources are allocated only for those chemical substances which have a potential to be discharged to receiving waters in concentrations of environmental or public health concern. This contrasts with the traditional broad spectrum gas chromatography (GC)/mass spectrometry (MS) scanning approach to wastewater characterization which consistently generates analytical data for many chemicals that have no potential of being discharged.
- IPC also encourages considerable communication and contact between industry and regulatory agency staff early in the permit development process. We believe that this enhanced level of communication will lead to the eventual development of more accurate and viable NPDES permits.
- IPC is also not limited in scope to any specific list of toxic pollutants, such as EPA Priority Pollutants or Michigan Critical Materials. IPC instead concentrates on those chemicals which are used, produced and discharged by the industrial facility being evaluated.
- IPC provides State/Federal regulatory agencies access to previously unavailable information concerning a facility's processes (e.g., detailed process descriptions, comprehensive lists of raw materials used, facility blueprints, etc.) which is, in some cases, imperative to the development of adequate NPDES permit conditions from a toxic substances control perspective.

- IPC provides State/Federal regulatory agencies with a standardized mechanism for evaluating the potential environmental impacts associated with new or modified process operations.

Limitations of Industrial Process Characterization

Our experiences with IPC have also revealed several of its limitations or weaknesses which should not be overlooked in this presentation.

- Perhaps the major limitation associated with IPC is the length of time required to perform a study at some industries. Several companies have indicated that the type of work associated with an IPC study requires the involvement of staff who are intimately familiar with their facility's operations. This staffing requirement inhibits industry from contracting the work associated with an IPC study to outside consultants. Since an industry must use key staff members, the cost-effectiveness of an IPC study will depend heavily on the amount of time those staff members are absent from their normal duties.
- It is imperative that adequate confidential information handling procedures be available before IPC can be seriously considered for use in a State/Federal regulatory agency's NPDES program. Adequate confidential information handling procedures must be in place before an industry can be expected to divulge proprietary process-related information during the initial phase of an IPC study.
- The absence of reliable analytical methods for some chemical substances which are discharged to receiving waters by industrial point sources inhibits the overall effectiveness of IPC. However, it should be noted that all wastewater characterization techniques are limited by this problem.
- Several industries have questioned whether the State of Michigan has the authority under statute and rule to require an NPDES permit applicant to perform an IPC study. MDNR believes that adequate statute authority for requiring dischargers to conduct an IPC study is provided in Section 308 and 402(a) of P.L. 95-217, the Federal Clean Water Act; State Act 245, Public Act 1929, the Water Resources Commission Act, as amended, being Sections 4, 5 and 7; and Part 21 of the Administrative Rules of the Water Resources Commission, promulgated pursuant to Sections 2 and 2(a) of the Water Resources Commission Act. U.S. EPA Region V staff have also assured MDNR that adequate statute authority exists to support the inclusion of IPC study requirements in industrial NPDES permits. It should be noted, however, that the statutory authority question has not yet been court tested in Michigan.
- The absence of sufficient aquatic toxicity data for many chemical substances which are discharged to receiving waters by industrial

point sources also inhibits the value of some IPC studies. This limitation becomes particularly important during the preparation of final analytical lists. Those substances which are considered to have the potential of being discharged but cannot be characterized adequately as to their aquatic toxicity have usually been included on final analytical lists by MDNR.

Summary and Recommendations

In closing, I would like to stress that MDNR's evaluation of IPC as a potential tool for use in permit development is only partially complete. Additional field verification of the IPC study format must be conducted, especially Phase IV (Quantitative Analysis). MDNR has completed IPC studies at two major chemical manufacturing facilities (BASF Wyandotte Corporation and Pennwalt Company) using a slightly different format from the one presented here. IPC studies are currently in progress at the SWS Silicones Corporation, Stauffer Chemical Company and Standard Products Company; and we expect to include IPC study requirements in the NPDES permits of four additional facilities in the near future. When this field verification work is completed, our Office will make its final recommendations to EPA and MDNR management regarding the value and potential uses of IPC in the NPDES permit development process.

Acknowledgement

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ATTACHMENT I

Phase 1 - Submission of Background Process-Related Information

For those processes which contribute wastewater to the Company's final effluent(s), the Company shall submit the following background information to the Department for review purposes:

1. Name and narrative description of each distinct facility process operation.
2. Method of production for each distinct facility process (campaign, batch, continuous).
3. A list, by process, of raw materials, trace contaminants of raw materials, trade name formulations, intermediates, intended by-products, unintended by-products, and products used or produced in or incidental to facility processes (chemicals used in laboratory quantities, less than 2 kg/month, do not need to be reported).
4. The amount (lbs), by process, of raw materials, trace contaminants of raw materials, trade name formulations, intermediates, intended by-products, unintended by-products and products used or produced in or incidental to facility processes.
5. The name, address, and phone number of the manufacturer, supplier or distributor of each trade name formulation used at the facility.
6. Toxicity data available for each raw material, trace contaminants of each raw material, intermediate, intended by-product, unintended by-product, product, and trade name formulation used in or incidental to each facility process (include Material Safety Data Sheets for trade name formulations).
7. Stoichiometry and general description, by process, of the chemistry involved for each chemical reaction (if any) used in product(s) synthesis.
8. A list, by process, of sources of process, contact quenching or cooling, unrecirculated noncontact cooling, and recirculated noncontact cooling wastewater, including air emissions control device wet scrubber wastewater.
9. The frequency of discharge, by process, for each source of process, contact quenching or cooling, and noncontact cooling wastewater.
10. A list, by process, of raw materials, trace contaminants of raw materials, intermediates, intended by-products, unintended by-products, products and active ingredients of trade name formulations which may be present in source wastewater(s).

11. A description of the actual pipe layout (above and underground) used to connect each process operation to the wastewater treatment system(s) and/or facility outfall(s). The location of all floor drains and vents in the process work areas should also be indicated.
12. A list, by process, of any wastewater sources discharged directly to the receiving water without treatment.
13. Analytical chemistry data available characterizing the composition of untreated wastewater effluent to the receiving water.
14. Analytical chemistry data available characterizing the composition of each individual process waste stream prior to treatment.
15. A list, by process, of wastewater sources treated prior to discharge to the receiving water.
16. Calculated or estimated flow volumes for each individual process waste stream, cooling water, and/or combined wastewater discharge.
17. A narrative description of each stage of the treatment system(s) employed.
18. A block flow diagram of the treatment system(s).
19. Analytical chemistry data available characterizing the composition of wastewater influent to and effluent from the treatment system(s).

GS/vls

PREDICTION OF ORGANIC
TOXICANTS IN CHEMICAL
INDUSTRY EFFLUENTS

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PREDICTION OF ORGANIC TOXICANTS IN CHEMICAL INDUSTRY EFFLUENTS

The prediction of the presence of toxic organic compounds in chemical industry effluents can provide useful information to both manufacturing and regulatory interests. The focusing of the prediction on toxic organic pollutants is an example of the general prediction of the organic composition of an effluent in terms of the classes of compounds that may be present. The following discussion illustrates the techniques used in predicting the presence of toxic pollutants and the potential uses of the predictive scheme.

In order to use a predictive process two primary subjects must be addressed; the methodology of the procedure and the specific objective of the prediction.

Figure 1 presents in graphic form the key areas to be addressed for defining both the methodology and the objective. The methodology of using predictive techniques is general and will likely not vary from one study to another. It contains three critical factors; identify a list of the chemical compounds of interest, a general concept of the toxicity of those compounds and a notion of the class of processes that may be represented by the compounds.

Prior to identifying the general processes by which the target compounds are made and their toxicity, they should be identified as to which existing chemical family they belong. This identification allows background data to be assembled for all similar products to create a library of knowledge containing all types of physical, chemical and toxicological data etc on the target compound. In essence, this effort information boxes that can be correlated with information developed through the subsequent prediction effort.

Next, some concept should be formulated as to the level of toxicity which will trigger the investigators interest. If moderate toxicity (acute or chronic) will stimulate someone's interest, then many more compounds whose presence will be predicted will have to be surveyed than if only highly toxic compounds are of interest. This definition of the level of toxicity defines to a large extent the magnitude of the effort in predicting the toxicity or treatability of an effluent.

In order to fully utilize the benefits of a predictive scheme the investigator should be able to define the generic processes which produce the target compounds as either a product or by-product. Since toxicity, treatability, etc are activity indicators which are dependent to at least some extent on functional groups present in the molecule, and those functional groups frequently have similar responses to the activity indicators, and the functional groups enter the molecule through an industrial process, the definition of the generic process will tie together the origin of the target compounds, their activity (in general) and perhaps their level of toxicity.

It is the generic process concept that allows the simultaneous correlation of the origin of compounds in effluents, their toxicity and general treatability. That correlation for any class of compounds is presently very poorly defined. The process of examining the universe in order to focus on those compounds made in commerce, which have some defined toxicity and are treatable by known technology, can only be described as an art.

As previously stated, after the general methodology of the study has been reviewed, the objectives should be carefully selected. For example, compounds of a specific class can be selected for study such as ethers, amines, carboxylic acids. To facilitate the searching or prediction of toxicity the Wisswesser line notation of sample compounds can be used. A level of toxicity for those compounds of interest should also be defined. Is the investigator concerned with acute or chronic effects, teratogenicity, carcinogenicity, etc. and at what general level? A third factor which will focus on the applicability of the compound class and toxicity is the distribution of the class of products throughout the commercial world.

Some compounds may not be produced in commerce and the study therefore be focused on the potential toxicity of an effluent from the production of a new chemical species. On the other hand, the target compound and species may be produced by selected facilities at limited locations, defining a limited area of concern for industry and the regulatory interests.

Having defined the need for a generic process descriptor as the common link between toxicity, treatability, and chemical production processes we need to examine what a generic process is and how it can be described in commercial use. Figure 2 indicates that a generic process is the kinetic or reactive portion of a product/process. A product/process contains three elements as shown; a raw material (feedstock), a generic process, and a product. The generic process links the raw material into and the product of a chemical process.

Figure 3 shows some additional information about generic processes. They are the means by which function groups (sometimes functional structures) are introduced into molecules or perhaps modify existing functional groups, to form new functional groups (alcohols and acids form esters). Some of the common functional groups are listed in the figure. Of those producing the largest number of compounds of toxilogical concern, chlorination probably ranks first. Note that the generic process does not define the process source of toxic effluent/waste/emission. That exercise is in its infancy and is usually defined as industrial process characterization or engineering analysis. The ability to do such an analysis or characterization requires the merging of chemical and chemical engineering expertise and will not be addressed here.

To further elaborate on the generic process concept, Figure 4 presents the chlorination of benzene in a narrative and mathematical context. As previously stated the generic process of chlorination relates the product, chlorobenzene, to the raw material, benzene. In contrast to the operation of the chemical industry, Figure 5 presents an example of a process from the steel industry. The production of iron results from the reduction of iron ore by carbon monoxide formed in-situ by the combustion of coke. The generic process in use is a form of chemical reduction.

At this point it is useful to point out the origin of the complexity of the organic chemicals industry. For the steel industry nearly all facilities which produce iron will utilize the basic process shown in Figure 5. Granted, there will be differences in practice from site to site due to the initiative of engineers to improve and adapt the process to special conditions. The iron-from-iron-ore industry which uses the one general process, reduction, is therefore homogeneous. In contrast, the organic chemicals industry uses approximately 40 generic processes. To further complicate matters the product of one generic process can be raw material to the same generic process producing new products. The feeding of iron to a blast furnace produces only iron, nothing new. The chemical industry contains an interlocking structure where the relationship of products to raw materials is best defined through generic processes. The interlocking nature of the industry can best be described as dendritic, denoting the thousands of interrelated compounds.

Returning to the sample prediction, Figure 6 lists some information supplemental to the generic process information. The commercial processes producing the compound(s) of interest may be defined. The generic routes to those compounds should can be defined and listed as part of the commercial process. As a matter of convenience, the investigator might estimate the type of waste discharges expected from the process. This does not mean extensive process analysis or characterization but only an estimate of whether the predominant yield losses will be to the air, water or solid media. An estimate of this type will become a critical need if risk assessment of the yield losses is essential.

Figure 7 provides some background on the nature of losses from a chemical process. If the process chemistry is viewed as producing a range of products and those products vary in molecular weight, then the sum of all products of all molecular weights equals the input to the process. For the most part the chemical species produced in the greatest yield are the

commercial products. When these are removed through conventional chemical process techniques, some species of all molecular weights are left behind as the potential environmental problem. The medium which the compounds enter is dictated primarily by molecular weight with those of low weight entering the air and the higher molecular weight materials becoming solid waste. Those compounds of median molecular weight which are water soluble become constituents of the process water effluent. There are obvious overlapping areas in this simplified scenario. It is critical to estimate, however, the medium of interest for the particular generic process since toxicity and risk factors may be dependent on the medium receiving the target compounds. The extent of pollution abatement control necessary and associated costs can be significantly affected.

The procedure outlined above has been accomplished by EPA for a defined group of compounds, the priority pollutants. Figure 8 summarizes the activities carried out during the study. Legislation defined for EPA the compounds of interest and characterized them as toxic under Section 307(a) of the Clean Water Act. Those compounds known as priority pollutants were classed according to functional group and the commercial processes were identified which could produce those chemicals as products or by-products. The resulting information was summarized according to the generic relationships between the processes and the target pollutants to provide a logical, concise representation of the commercial universe. Unfortunately, this study did not require the screening of the processes for toxicity of an anticipated effluent. The legislative effort dictated the removal of the priority pollutants to a level defined by Best Available Technology. The procedure is applicable, however, should the investigator provide a substitute screening scale for toxicity similar to that provided by Section 307(a) of the CWA.

The results of the study for the priority pollutants are shown in Figure 9. Note that for the 88 organic priority pollutants, a matrix which is 6 x 6 with only limited entries is required to define the origins of the target compounds. A majority of the chemical industry's processes do not, in fact cannot, produce priority pollutants. The procedure has been

successful, therefore in defining the universe of concern. Those establishments which do not use the generic process listed in Figure 9 would not be suspected to discharge effluents containing priority pollutants which originate as products or by-products of the process. Further investigation could remove from concern those processes which do not use the raw materials named in the figure.

In conclusion, we should note that it is easy to lose sight of the potential benefits of the generic concept of the chemical industry. Normally, an investigator will intuitively correlate toxicity, treatability, and other activity measures with the generic class of compounds. The technique is in reality a means by which chemical structure is expressed through a generic process and activity is measured by the occurrence (presence), toxicity or treatability. Formalization of the technique is not essential, but as a means of communication and organization between scientific disciplines, it provides an invaluable resource.

Figure 1

PREDICTION OF TOXICANTS IN CHEMICAL INDUSTRY EFFLUENTS

METHODOLOGY

1. INDUSTRY PRODUCTS
2. TOXICITY OF TARGET COMPOUNDS
3. USE OF GENERAL PROCESS CONCEPTS

OBJECTIVE

1. SPECIFIC COMPOUND OR FUNCTIONAL GROUP
2. TOXICITY
3. PROCESS ORIGIN

Figure 2

GENERIC PROCESSES AND
PRODUCT/PROCESSES

PRODUCT/PROCESS REQUIRES DEFINITION
OF THREE ELEMENTS

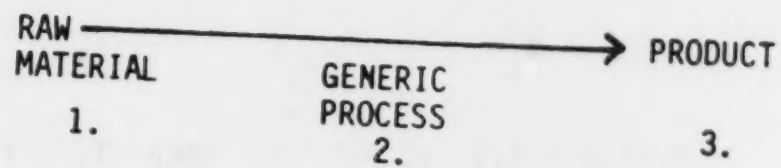
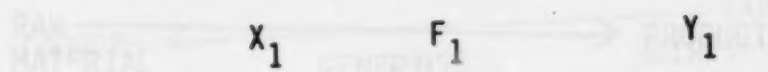


Figure 3

CHEMICAL INDUSTRY AND OTHER
INDUSTRY PRODUCT/PROCESSES

1. MATHEMATICAL REPRESENTATION OF
A CHEMICAL PRODUCT/PROCESS



$F_1(x_1) = y_1$; if $x_1 = y_1$ then $y_1 = y_2$, etc.

Figure 4

2. IRON

iron ore, coke, $\xrightarrow{\text{heat time}}$ iron
limestone F_2 Y_2
 X_2

3. FOR CHEMICALS $F = 40$

X or Y = thousands

Figure 5

**FINDING POLLUTANTS IN
CHEMICAL PROCESS WASTES**

1. Commercial process reviewed
2. Generic process assigned
3. Look at all waste discharge points
in the process.

Figure 6

COMMERCIAL PROCESSES
LOSSES TO VARIOUS MEDIA

1. PRODUCT LOSSES BY MOLECULAR WEIGHT

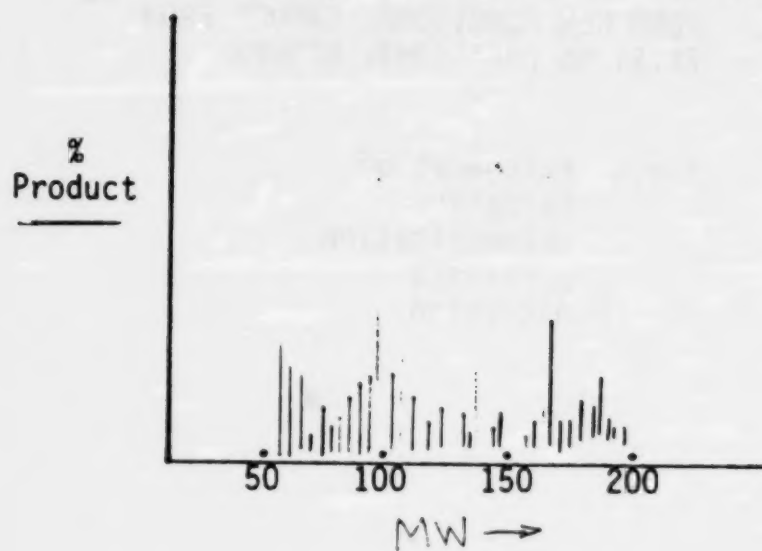


Figure 7

GENERIC PROCESSES

1. INTRODUCE FUNCTIONAL GROUPS OR
SUBSTITUENTS INTO HYDROCARBONS
2. FORM NEW FUNCTIONAL GROUPS FROM
EXISTING FUNCTIONAL GROUPS

i.e., halogenation
oxidation
polymerization
pyrolysis
nitration

Figure 8

TARGET POLLUTANT

APPROACH-PROCEDURE

1. Identify commercial processes having groups or molecules of interest
2. Study the generic process of interest with various raw materials
3. Select the combination of generic process, raw material, and commercial production to focus the survey.

Figure 9

PROCEDURE APPLIED FOR
PRIORITY POLLUTANTS

Important
Raw Materials

aromatics
ethylene
propylene
amilines
phenal(s)
methane

Important
Generic Processes

oxidation
chlorination
nitration
diazotization
reduction

Figure 10

USE OF THE TECHNIQUE

1. Qualitative prediction of specific pollutant discharge
2. Simplified (focused) analytical programs
3. Risk assessment based on functional groups or specific compounds.



**Process Evaluation and Modification
to Identify, Control, and/or Eliminate
Toxicants in Wastewater From a Coal Tar
Processing Plant**

S. A. Visnic

Industrial Toxicant Workshop

June 15, 1982

Process Evaluation and Modification to Identify, Control
and/or Eliminate Toxicants in Wastewater from a Coal Tar

Processing Plant

My presentation today is entitled "Process Evaluation & Modification to Identify, Control, and/or Eliminate Toxicants in Wastewater from a Coal Tar Processing Plant." I will present Allied's experience with toxic pollutant control from our coal tar products facilities.

I'll first give you a brief description of our business group, the plants we operate, and the processes we use. The tar products group is a business area within Allied Chemical Company, this representing the chemical operations of Allied. The tar distillation business began in 1857 by the Barrett Company, which was one of five companies which later formed Allied Chemical Corporation.

Allied still operates 3 tar plants. These are located in Ironton, Ohio; Birmingham, Alabama; and Detroit, Michigan. These facilities produce a wide range of products. Among them are naphthalene, anthracene, refined tars, creosote oils, and coal tar pitch.

The coal tar process basically involves distillation to separate coal tar into its different boiling fractions by varying the temperatures and pressures in the system. This flowsheet will show the basic tar distillation process.

Because coal tar from coking operations is our feedstock, the wastewaters we generate are similar to coke plant effluents and may contain similar type pollutants. These may include phenolics, cyanide, ammonia, thiocyanate, benzene, toluene, and a number of polynuclear aromatic hydrocarbons, such as naphthalene and anthracene.

Now we'll get into the process modification part of my presentation. I'll briefly review a general procedure for evaluating a system under consideration. The 5 basic steps include:

- Problem observation
- Data gathering
- System evaluation
- Process modification
- End-of-line treatment

The first step to start the procedure is that of observing a problem. This could be in the form of permit violations, new regulations, complaints, or just high operating costs.

After it is verified that a problem exists and a modification or additional treatment may be necessary, all pertinent data should be obtained. This includes process-type data as well as analytical data. Another key item in the data-gathering step is for the people involved to learn the system. In order to modify a process, you must know how a system works and why it behaves in this manner.

By learning how and why the system works and bringing all available data together, the system can be evaluated to determine what is required to meet current and future regulatory and operating needs. Then, if possible, process modifications can be made to meet these requirements. Key items to consider as modifications are the possibilities for recycle or recovery. This can result in substantial economic benefits.

After the possibility of modifying the process is evaluated and found to be infeasible, then end-of-line treatment can be investigated.

I'll now review several of the process modifications and additions we've made at our tar plants over the past several years.

Several modifications have been made in the tar distillation process. The majority of our distillation operations are high temperature-vacuum processes. These vacuum systems were the source of several modifications. Steam ejectors have been the most common method of producing vacuum conditions. We have in the past utilized multi-stage jet systems with direct contact barometric condensers. In this type of a condensing system, the incoming process vapors are in contact with the cooling water and this gives a contaminated water stream of large quantity.

By converting to an indirect contact system with surface condensers, the cooling water and the process stream are on separate sides of the condenser. The cooling water is part of a closed cooling tower system and the process stream is only steam condensate and condensibles from the process.

Two vacuum systems were modified in this manner. By separating the streams, the volume of contaminated water was reduced and could be removed from the plant's outfall and handled by the existing recovery system.

The following results were obtained by modifying these systems:

2-stage system

100 PPD phenolics from outfall
96,000 → 2000 GPD flow

3-stage system

0.5 - 10.0 PPD CN from outfall
50,000 → 3000 GPD flow

A similar multi-stage system was replaced with a mechanical liquid ring vacuum pump system. The vacuum pump uses a liquid as a seal to isolate the incoming process vapors and create the vacuum. Normally water is used as the sealing medium, but this only creates additional contaminated water. We have utilized a non-volatile coal tar solvent for use as the liquid seal. With the coal tar solvent, the incoming process vapors are condensed and absorbed by the seal liquid. Upon saturation with the condensed process vapors, the seal liquid is recycled back as feedstock.

This installation eliminated all contaminated water discharges and reduced the plant's cyanide loading by one-third as well as a reduction in polynuclear aromatic hydrocarbons. The system was installed for \$90,000 and reduced energy consumption by \$23,000/year by converting from steam to electric. Another added benefit was a 20 ton VOC air emission credit.

Process modifications have also been made in the anthracene refining process. This process consists of a series of crystallization steps using both water and a proprietary solvent to produce refined anthracene from an anthracene-rich creosote oil.

The first step of the process uses water as the crystallizing medium. The process originally was a continuous once-through direct contact counter-current crystallization in a crystallizer tower with only oil removal prior to the water being discharged.

This process was later modified to meet a reduced phenolic limit by converting to a closed process water recycle system with an oil removal step and an indirect cooling system for cooling the process water. This resulted in only periodic discharges of the process water as the reduced volume of contaminated water could be handled by the plant's recovery system.

This system was again modified and recently converted to indirect crystallization. This uses a closed cooling tower loop and a crystallizer equipped with cooling coils and agitator. This system resulted in less process upsets, better system control, increased product yields, as well as no discharge of process wastewater.

Summarizing the results of these modifications:

Continuous Direct Crystallization (w/continuous discharge)

15 - 75 PPD phenolics

15,000 - 20,000 GPD Flow

Closed Loop Direct Crystallization (w/periodic discharge)

<1 PPD Phenolics

<1000 GPD Flow

Indirect Crystallization

No discharge of process water or phenolics

The next case history did not yield a reduction in pollutants to surface waters, but the principle of process modification still holds true.

Part of the anthracene refining process involves several solvent recovery steps. The first step is a batch distillation to recover a majority of the spent solvent. The waste stream from this distillation is a water/solvent

azeotrope which could not be separated further in this process. The azeotrope stream and contaminated stormwater runoff together form a wastewater stream which contains from 1 to 10% solvent.

This stream was disposed of in the past by deepwell injection. Because of the rising cost for the disposal of this stream, an alternate means of treatment was investigated.

We were able to modify an idle steam stripping system to separate this solvent/water mixture by steam distillation. The solvent-free water was then able to be discharged.

This installation had a capital cost of \$65,000 for modifying the idle equipment. It reduced operating costs by \$130,000/year - \$65,000 in disposal costs as well as recovering 125,000 lb/year of solvent worth \$65,000/year.

Several minor modifications as well as additions were made to the oil removal system at one of our facilities. Because of capacity increases in several processing areas, additional quantities of oil, in particular, emulsified oils were present in the plant's outfall. The existing API gravity separator was not adequate to handle this increase in emulsified oils.

Oil coalescing plates were added to the separator as well as minor modifications to the automatic skimming/recycle system. Some reductions in oil and grease were attained, but additional removal was still required.

Small quantities of water treatment polymers were then added to the turbulent zones of the water transport system. These chemicals aided in breaking the emulsion and allowed the settled oils to be recovered in the API separator for recycle back to feedstock.

The polymer addition resulted in the removal of an additional 40% of the remaining oils. You can see from the graphs the improvements the system made compared with oil and grease values prior to the chemical addition.

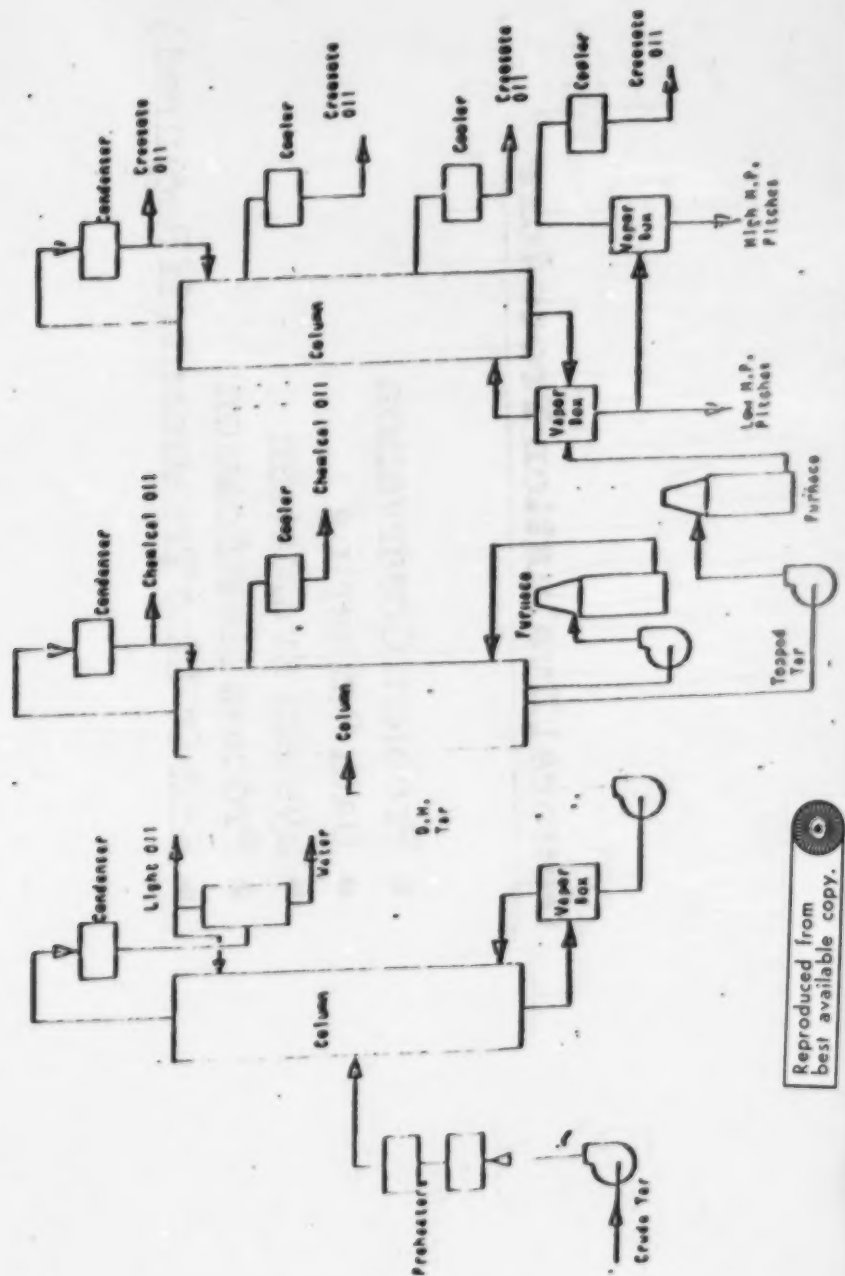
Because base-neutral priority pollutants, including PAH's, have a high solubility in coal tar oils, a reduction in O & G results in a corresponding reduction in these compounds. The reductions range from 65% to essentially 100% for naphthalene with most values greater than 90%.

As you can see from these examples, process modification can be an attractive method for eliminating or reducing the discharge of toxic pollutants. Modifications which include some type of economic benefit, such as recycle, recovery, or energy savings, can substantially cut operating costs, and sometimes an installation can be justified solely on this benefit.

Oftentimes, a modification is all that is needed. Other times, end-of-line treatment may also be necessary. But process modifications should always be investigated because a process change may substantially reduce

both the capital and operating costs of the end-of-line treatment. The process change then becomes a "pretreatment-type" step. So together or alone, process modification can be a worthwhile alternative.

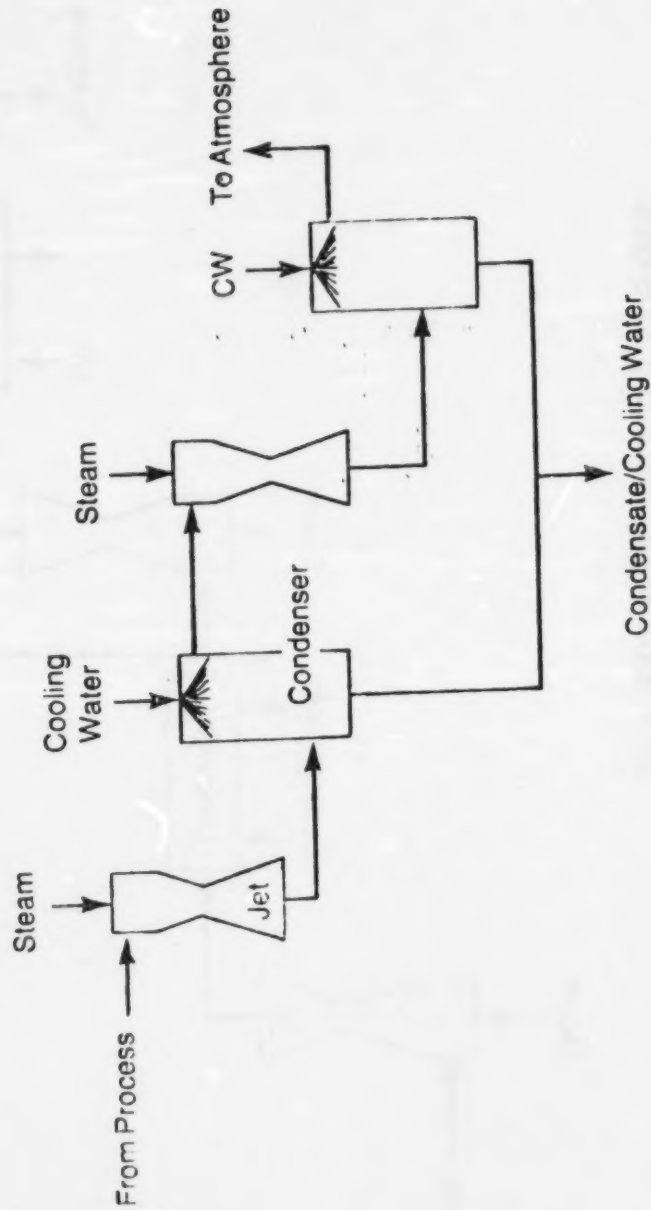
One thing I might add is that all process modifications do not always reduce the level of pollution. Great care should be exercised in evaluating all modifications and revisions to existing processes. The potential for increasing pollution is as great, if not greater, than the potential for less pollution.



General Evaluation Procedure

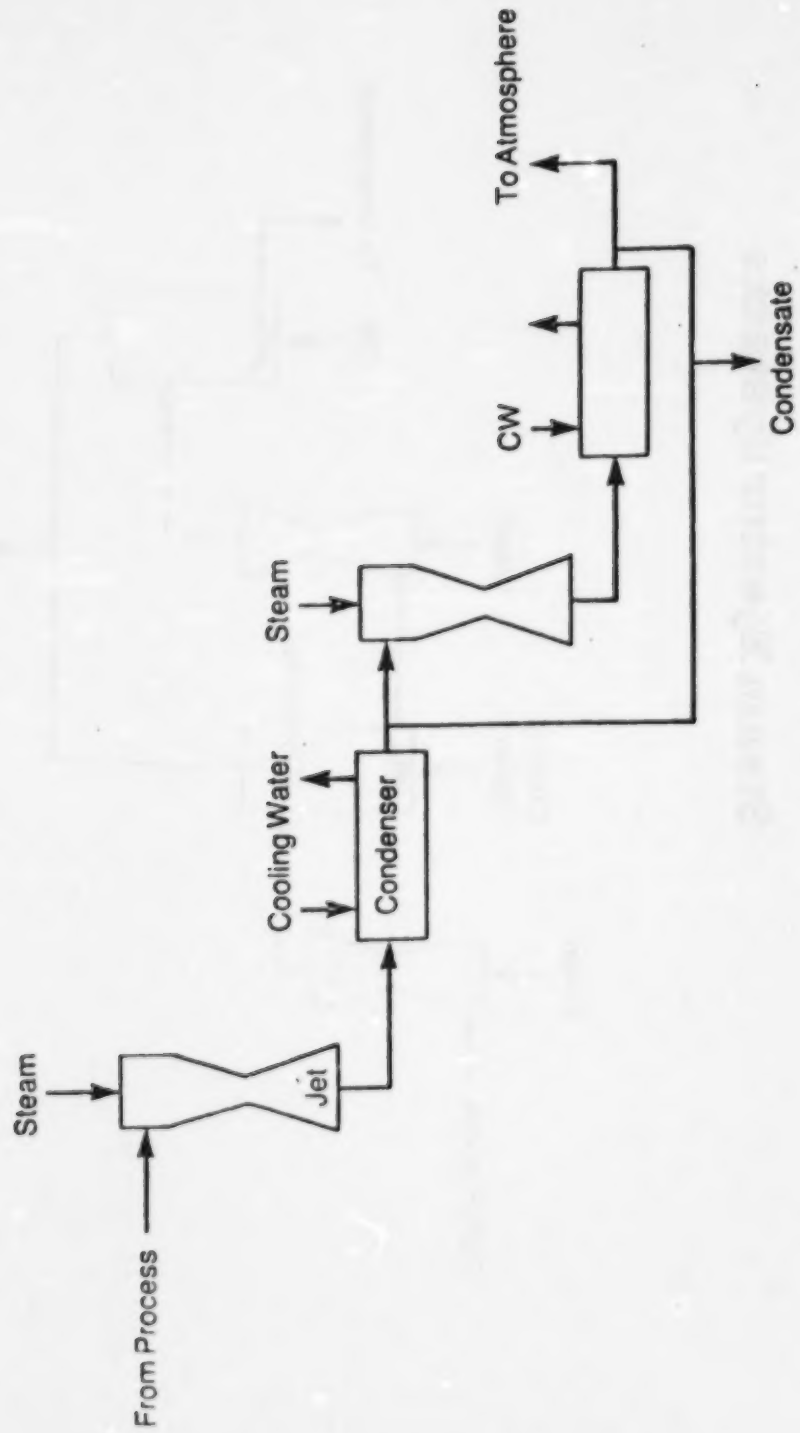
- Problem Observation
- Data Gathering
- System Evaluation
- Process Modification
- End-Of-Line Treatment (If Required)

Steam Ejector Systems



Direct Contact

Steam Ejector Systems



Indirect Contact

Steam Ejector Systems

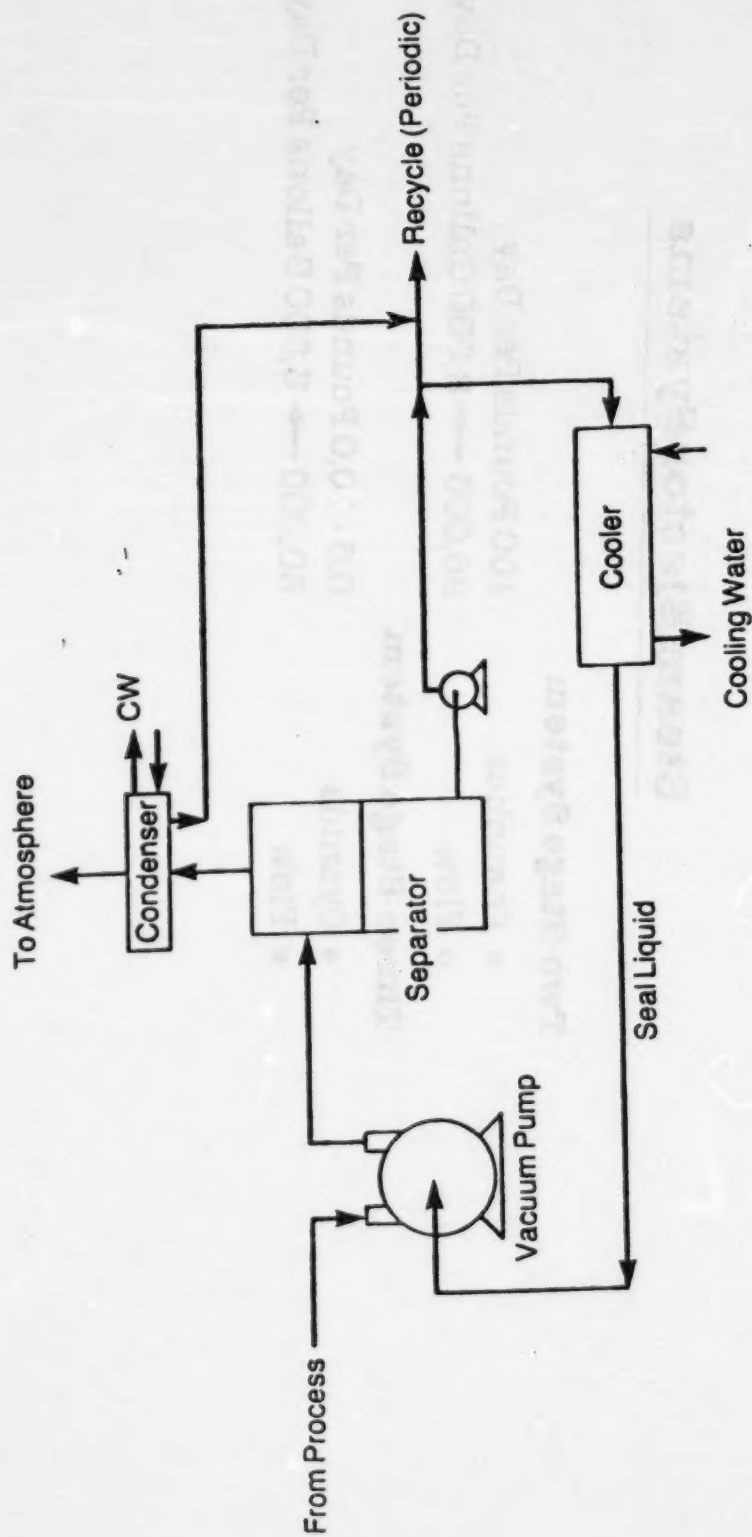
Two-Stage System

- Phenolics
 - Flow
- 100 Pounds Per Day
96,000 → 2,000 Gallons Per Day

Three-Stage System

- Cyanide
 - Flow
- 0.5 - 10.0 Pounds Per Day
50,000 → 3,000 Gallons Per Day

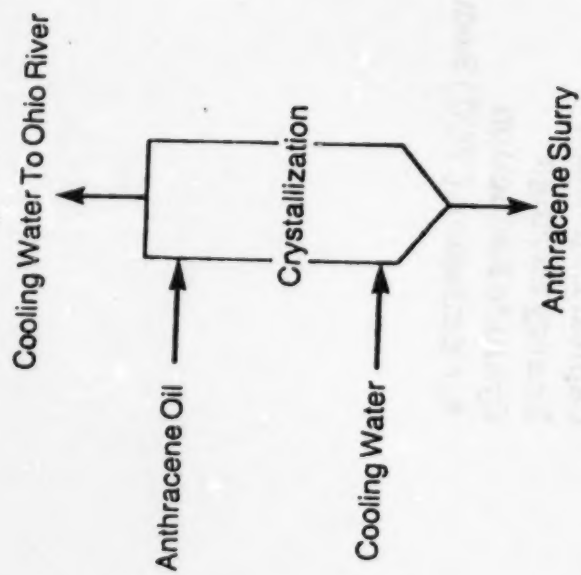
Mechanical Vacuum Pump System



Liquid-Ring Mechanical Vacuum Pump System

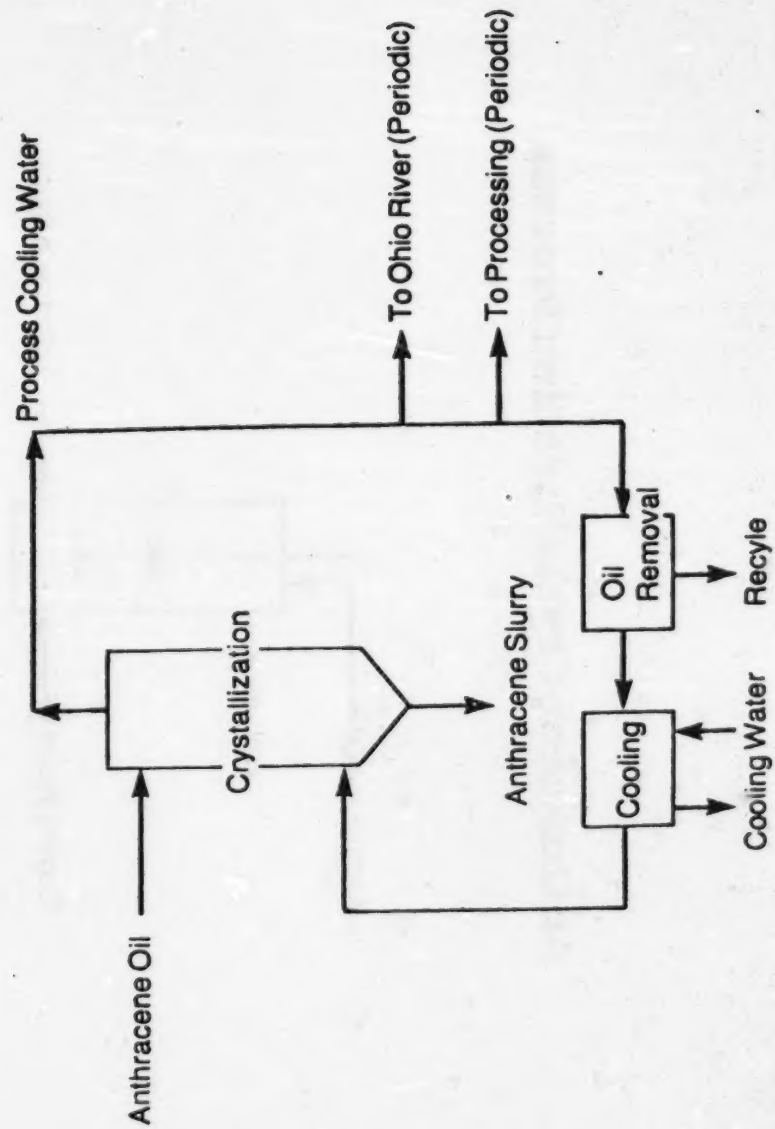
Capital Expenditure	\$90,000
Energy Savings	\$23,000 Per Year
Cyanide Reduction	33%
Air Emission (VOC) Reduction	20 Tons Per Year

Anthracene Crystallization Process



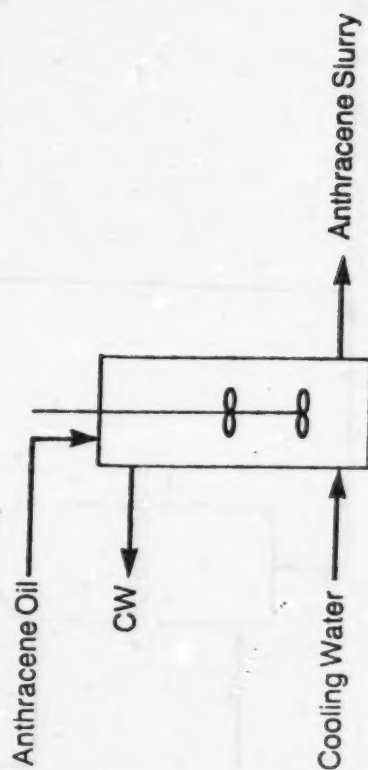
Continuous Discharge

Anthracene Crystallization Process



Periodic Discharge

Anthracene Crystallization Process



No Discharge

Anthracene Crystallization Process

Continuous Discharge

- Phenolics 15-75 Pounds Per Day
- Flow 15,000 - 20,000 Gallons Per Day

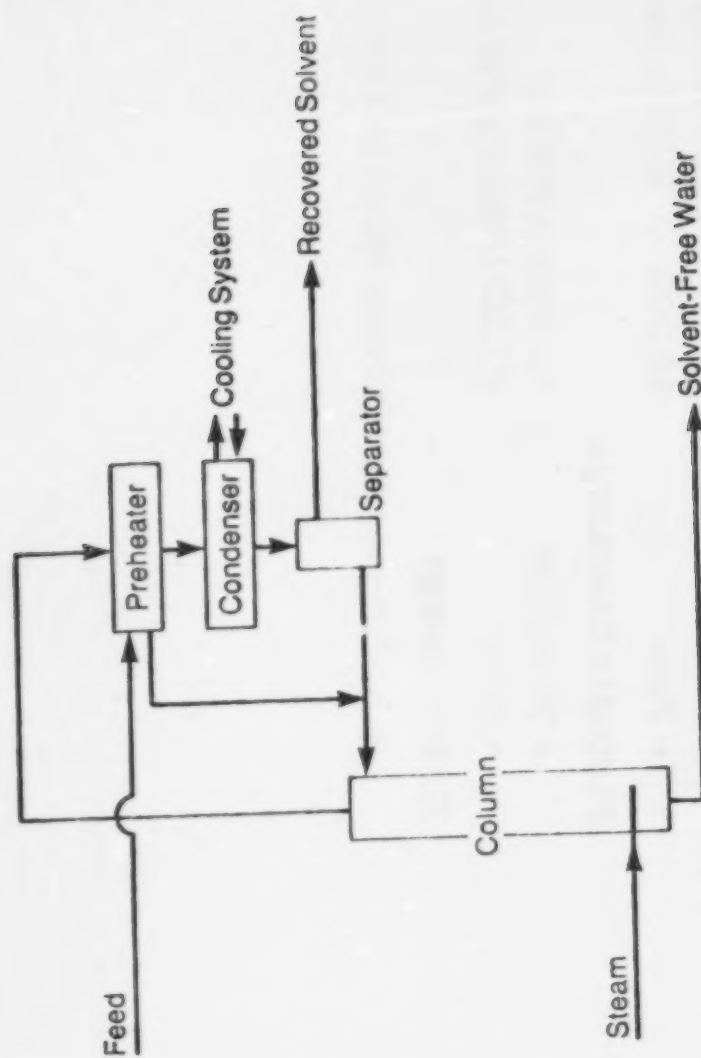
Periodic Discharge

- Phenolics <1 Pound Per Day
- Flow <1,000 Gallons Per Day

No Discharge

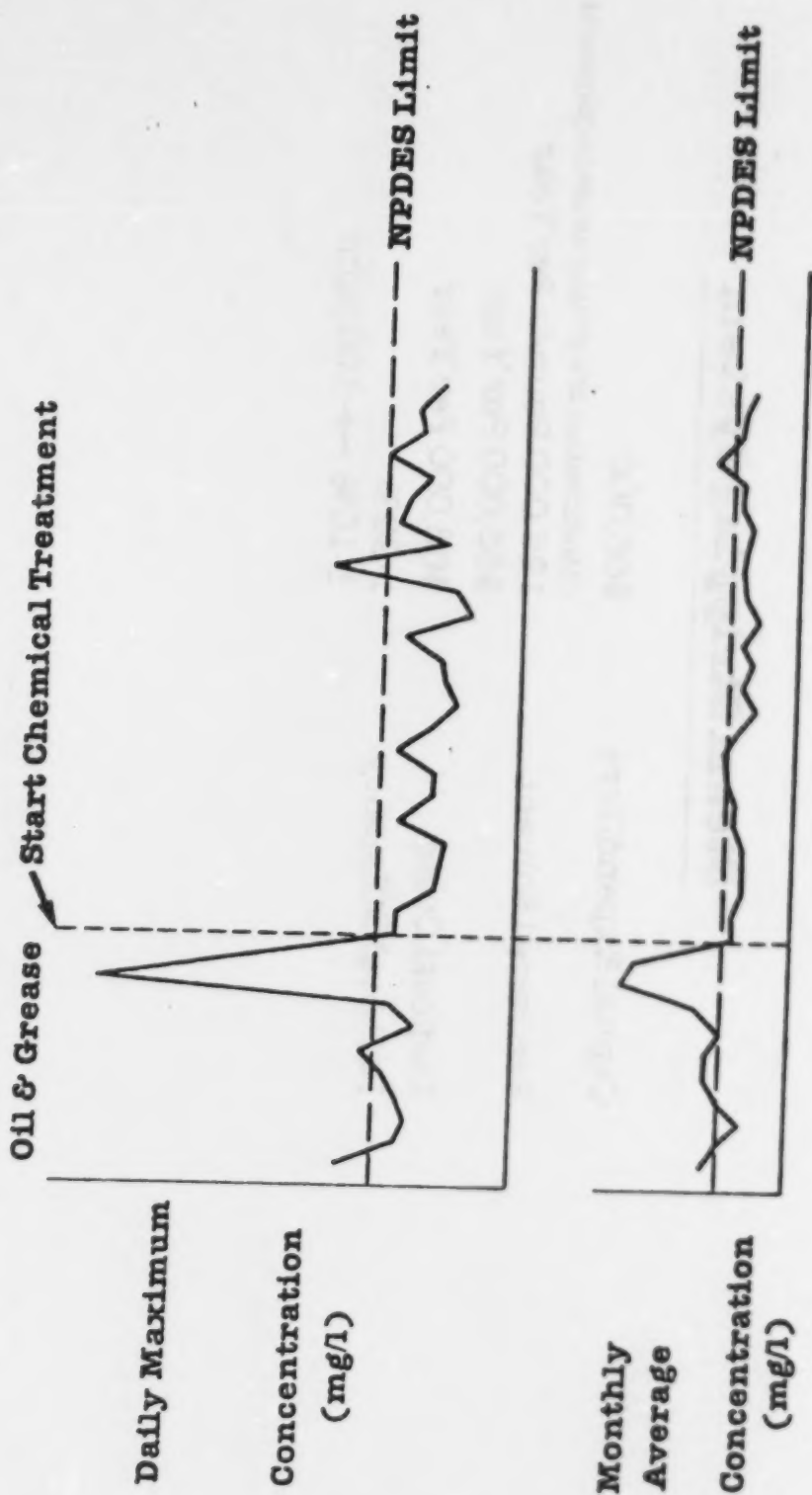
- No Discharge of Process Water or Phenolics

Steam Stripping System



Steam Stripping System

Capital Expenditure	\$65,000 (Modification of existing unused equipment)
Recovered Solvent	125,000 Pounds Per Year
	\$65,000 Per Year
Disposal Costs	\$65,000 Per Year
Removal Efficiency	>99% 1-10% → 100 ppm



Base-Neutral Compound Reduction Via Chemical Treatment

Acenaphthene	98%
Fluoranthene	96
Naphthalene	100
Benzo (a) Pyrene	65
3,4 Benzofluoranthene }	
Benzo (k) Fluoranthene }	69
Chrysene	
Benzo (a) Anthracene }	91
Acenaphthylene	99
Anthracene }	
Phenanthrene }	99
Fluorene	99
Pyrene	92

Environmental Cost Assessment:
A Computer-Facilitated Approach

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ABSTRACT

One of the tenets of pollution abatement and control strategy is that the most cost effective and efficient approach is the prevention or elimination of the pollution source itself. An important means of accomplishing this is through early identification of the potential impact that process wastes can have on the environment, and through early interaction with process chemists and engineers during the actual process development phase. It is here that input regarding the environmental abuse potential of a process can aid in significantly reducing the ultimate waste load generated, since the chemistry and process may still be changing and alternative routes and strategies can be examined most readily. However, a major difficulty with this approach to pollution management is the lack of adequate tools for this early assessment of the environmental aspects of a process. During the development phase, while a process is continually changing, detailed waste stream characterization would be unduly expensive. Therefore decisions on the nature and potential problems associated with the waste streams must be based on material balance information coupled with chemical judgment of the nature, types, and quantities of possible by-products.

This paper will discuss the translation of this type of information into a usable, quantitative measure of the potential treatment costs associated with process waste streams via a user-oriented computer program. Wastes are classified into 18 major categories, with sub-classes determined by user responses to program queries regarding the presence or absence of particular constituents. The various treatment trains which can be envisioned for each waste are then derived from combinations of unit processes or disposal options. The operating parameters of the options and complete trains are then determined for each unit and train for a given flow of waste and production rate. The program gives flexibility in examining the effects on cost of changes in waste composition, amount generated per unit of product, and of product production rate. Thus, it not only serves as an order-of-magnitude cost estimate for the environmental aspects of a process, but also allows changes or alternatives in chemistry and/or processing which can affect the waste stream characteristics to be readily evaluated in cost terms.

While the emphasis today in the pollution control area is away from traditional end-of-pipe treatment to in-process treatment, process modification, and pollution reduction, our philosophy and approach is to take that concept even further back and to deal with pollution problems during the actual process development phase itself. This involves interacting with the process development chemists and engineers from the inception of a development project to eliminate and prevent pollution before it becomes a problem. One of the difficulties associated with this approach, however, is that development chemists are traditionally not concerned with the waste streams generated by their processes. The challenge therefore becomes the development of innovative tools to provide information which they can use to choose between the many alternative chemical and engineering strategies that are possible in a given chemical synthesis. In trying to quantify the environmental aspects of a process so that this aspect can be fed-back to the development scientists, we initially conceived a very simple approach, which is called "a preliminary comparative method for assessing environmental impact." This involves two ideas: the first is a waste index (WI), which is simply the amount of waste that is generated per unit of product. Frequently many of the chemists involved in process research and development are unaware of the vast quantities of solvents and aqueous solutions which are used in processing and purifying the product and which must eventually be disposed in commercial practice. It is not uncommon for a process to generate 500-1000 times as much waste as product, so consideration of this aspect of a process, and efforts to reduce the waste load generated, are a necessary first step to pollution abatement.

The other idea in the preliminary method is to couple the waste index with a difficulty factor (DF), which essentially rates different types of streams. These two factors can then be multiplied to yield an "environmental impact" (EI) number for a chemical step or sequence, where

$$EI = WI \times DF$$

$$\sum EI = \sum (WI \times DF)$$

The first step in using this method is to determine an estimated material balance for the chemical step or sequence, as illustrated in Figure 1. The top box shows the raw materials used, and the middle and bottom boxes show the individual waste streams that are generated in the synthetic step. Given that typical processes may involve 10-15 such steps, the waste burden can be quite substantial.

79	68	1402	119	36	2344	36	1452	512
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(2250	92	26	78	18	159	122	68	13
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$$\begin{array}{r} \text{Total: } 2825 \text{ Kg} \\ \hline \text{W.I.} = 28 \text{ D.F.} = 5 \text{ E.I.} = 141 \end{array}$$

(280	59	11)
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$$\begin{array}{r} \text{Total: } 386 \text{ Kg} \\ \hline \text{W.I.} = 3.9 \text{ D.F.} = 3 \\ \hline \text{E.I.} = 12 \end{array}$$

(1335)	(830	107)
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$$\begin{array}{r} \text{Total: } 1335 \text{ Kg} \\ \hline \text{W.I.} = 13.4 \text{ D.F.} = 3 \\ \hline \text{E.I.} = 40 \end{array}$$

$$\begin{array}{r} \text{Total: } 1282 \text{ Kg} \\ \hline \text{W.I.} = 12.8 \text{ D.F.} = 3 \\ \hline \text{E.I.} = 38 \end{array}$$

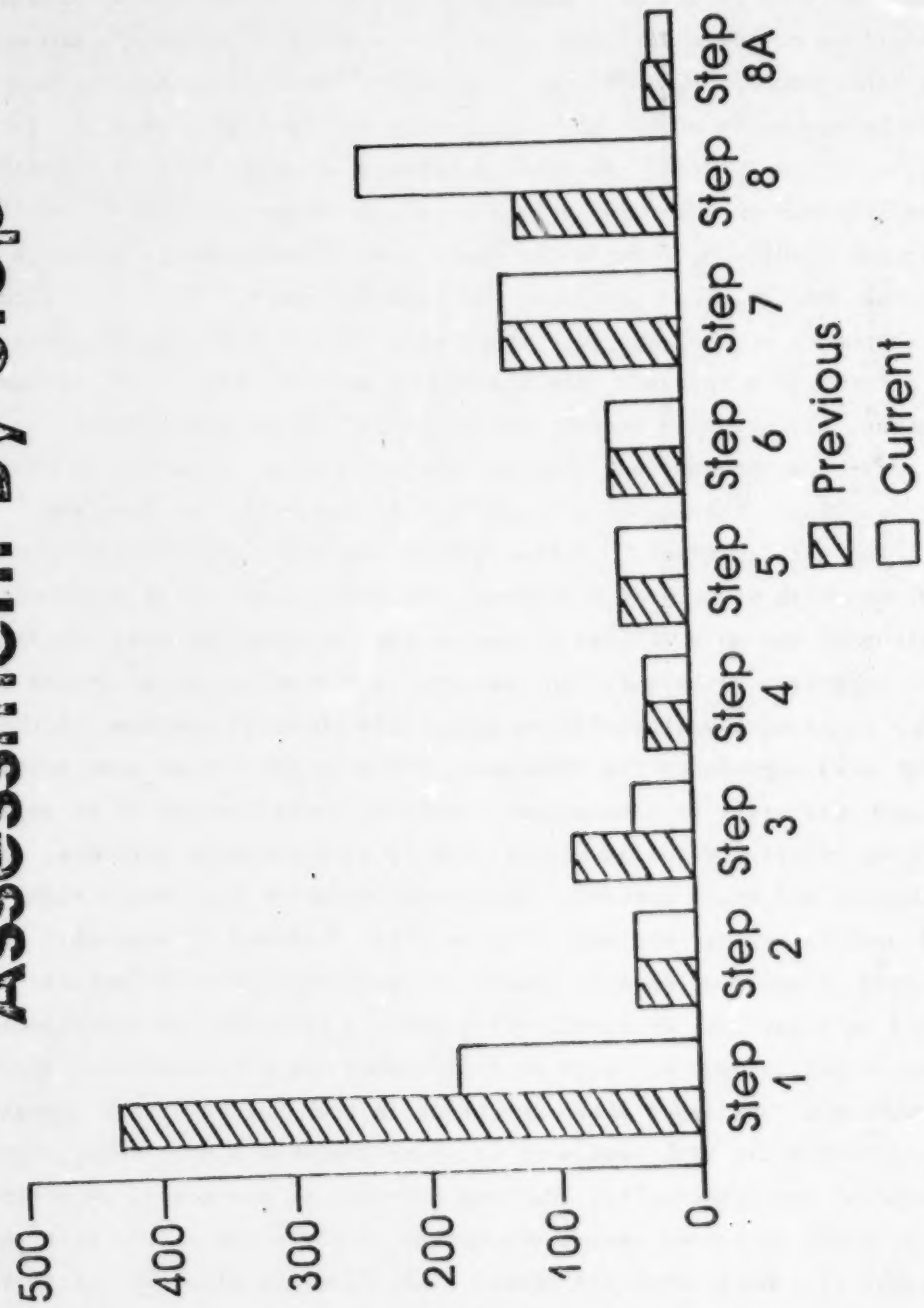
80	110
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In each box, the waste generated was totaled, and the waste index determined by dividing by the total product produced. Each stream was then assigned a difficulty factor, which is a qualitative assessment of the degree of difficulty associated with treating or dealing with the stream. The environmental impact number is then generated. Examination of this number for a typical process allows comparison of the individual steps of the process. Figure 2 shows two different synthetic routes by the steps. The shaded boxes represent the previous route used for the synthesis of the chemical, while the open boxes are the improved route. Originally the process generated a tremendous waste load in the first step. Once this information was relayed back to the development chemist, modification of the reaction conditions reduced the waste load significantly, although subsequent process modifications increased the load in step 8. This then focused attention on that step as the next to examine with regard to minimizing environmental impact. Also with this approach, the individual step EI numbers can be summed over the process, illustrating overall environmental impact comparisons, as shown in Figure 3. As a first approximation, this preliminary method is useful in process assessment for focusing attention on potentially serious pollution problems.

However, in order to derive a more realistic quantitative evaluation of the environmental aspects of a process, the difficulty factor scale was changed into a scale that not only defined a generic type of waste stream, but also assigned to it a treatment technique. For example, the simplest waste stream is an aqueous waste containing essentially no detectible chemical species. Although there is no associated representative treatment, there is still some cost involved since the stream must still be discharged. Another classification is an aqueous waste containing relatively low levels of readily biodegradable organics, such as acetic acid, methanol, and ethyl acetate. Here representative treatments might be dilution followed by aerobic biological or dilution followed by anaerobic biological treatment. A waste stream described as readily recoverable non-toxic organic solvent wastes could be dealt with by distillation under a given set of conditions, while non-toxic organic solvent wastes could be incinerated using conventional incineration and scrubbing technology. A waste prevalent in the pharmaceutical industry is an aqueous waste containing high levels of non-biodegradable and/or toxic organics and high levels of inorganic salts. For the purposes of our model, we propose filtration followed by activated carbon adsorption of the organics and salt removal by reverse osmosis or ion-exchange. The stream after possible dilution, could then be discharged to a conventional biotreatment facility. An alternative, albeit an expensive one, is incineration followed by wet scrubbing. As part of our strategy, of course, we want to be able to point out costs associated with alternative technology.

FIGURE 2

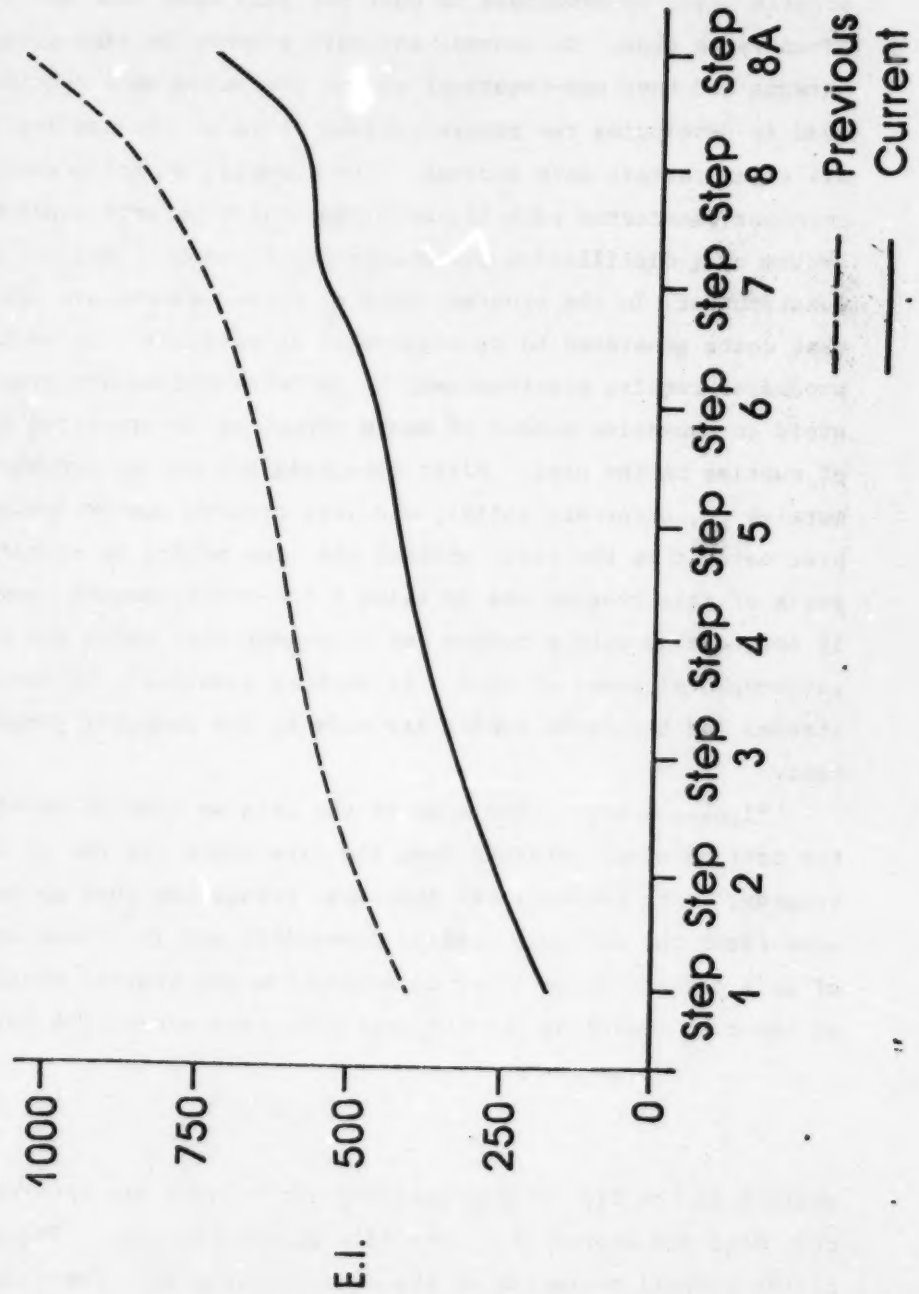
Preliminary Waste Load Assessment By Step



E.I.

FIGURE 3

Preliminary Waste Load Assessment By Process



In all, we defined 18 classes of generic wastes and potential treatment schemes which involved 22 separate unit processes. The aim was then to develop costs for each of these processes and then pull them together using a computer program which we developed to cost not only each unit but the entire train for any given waste type. Of course, any unit process is also going to generate waste streams and have pre-treatment and/or post-treatment requirements. The strategy used in developing the program allows it to do the costing automatically, taking all these factors into account. For example, an incinerator would have to have a scrubber associated with it, or biological treatment would need a prefiltration system or a distillation pre-treatment, depending upon the particular stream constituent. In the program, many of these aspects are already defined in order that costs generated be as comparable as possible. In addition, many of the unit processes require pre-treatment if certain species are present, so in order to avoid an excessive number of waste types, we incorporated into the program a series of queries to the user. After obtaining answers to a number of questions regarding metals, pH, suspended solids, etc., the program can automatically assign the necessary pretreatment to the train without the user having to specify it. One of the major goals of this program was to allow a non-environmental chemist or engineer to use it and come up with a number for treatment cost which was reasonable from an environmental point of view. As much as possible, the decisions concerning waste streams and treatment trains are made by the computer program and not by the end-user.

Figures 4 and 5 show some of the data we used in developing the costs. All of the cost data was obtained from the literature for the 22 unit processes and the program, using conventional indexing, brings the cost up to current dollars. In some cases the data was readily accessible and in others we had to do a fair amount of data dissection in order to assess how the costing would actually be done. All of the cost functions for the unit processes are of the form

$$Y = A Q^B$$

where Q is the flow in gallons/day, and A and B are determined from literature cost data and stored in a data file in the computer. Figure 6 shows a schematic of the overall operation of the computer program. The main information specified by the user is the waste type. These are listed by the program and are designed so that a typical user could define, on the basis of a preliminary material balance, the particular waste type to be costed. This information, along with parameters such as production rate and the amount of waste generated per unit of product, allow

Figure 4. Construction Cost for
Conventional Activated
Sludge Process with Diffused
Aeration

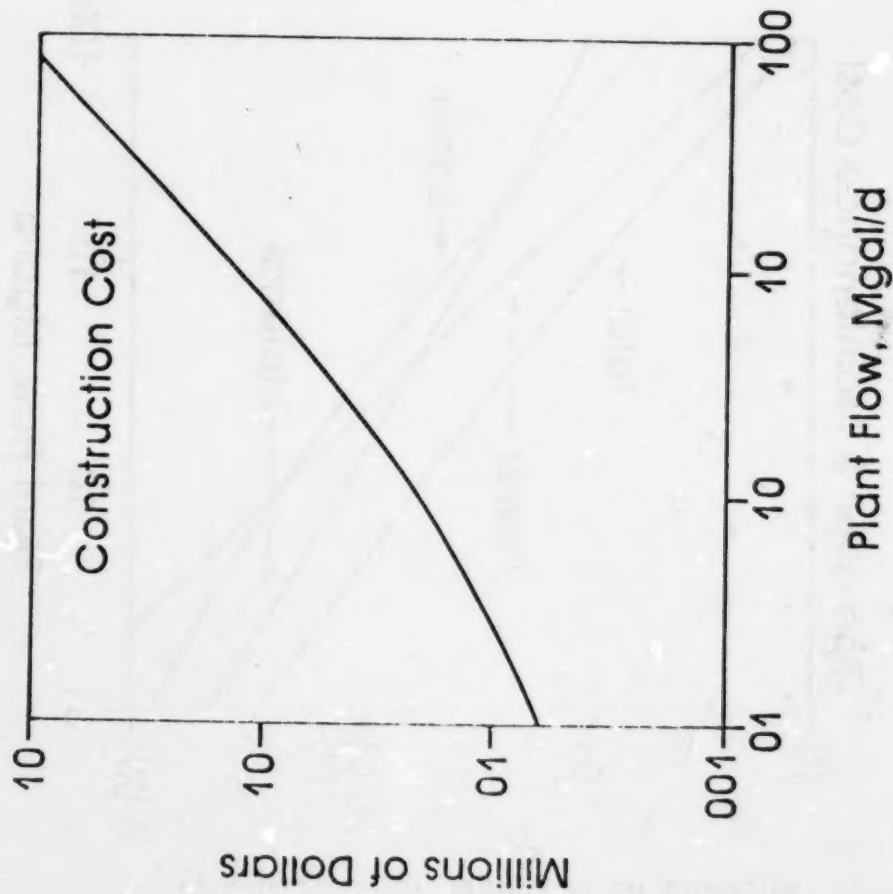


Figure 5. Operation and Maintenance Cost for Conventional Activated Sludge Process with Diffused Aeration

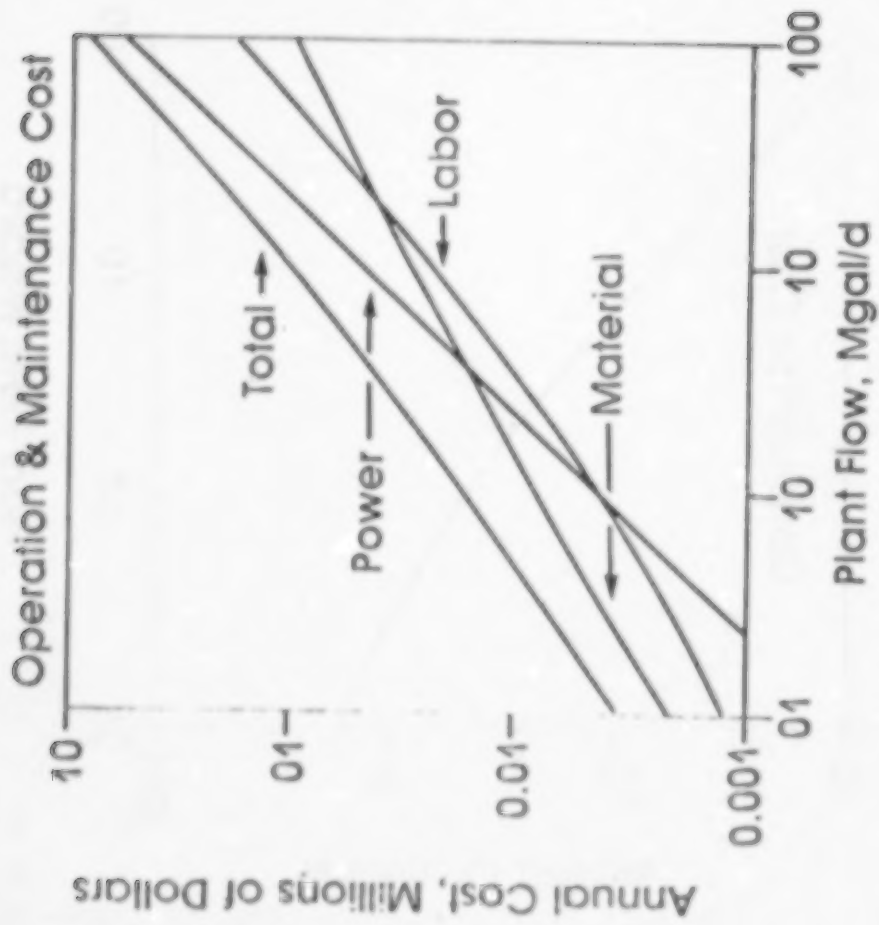
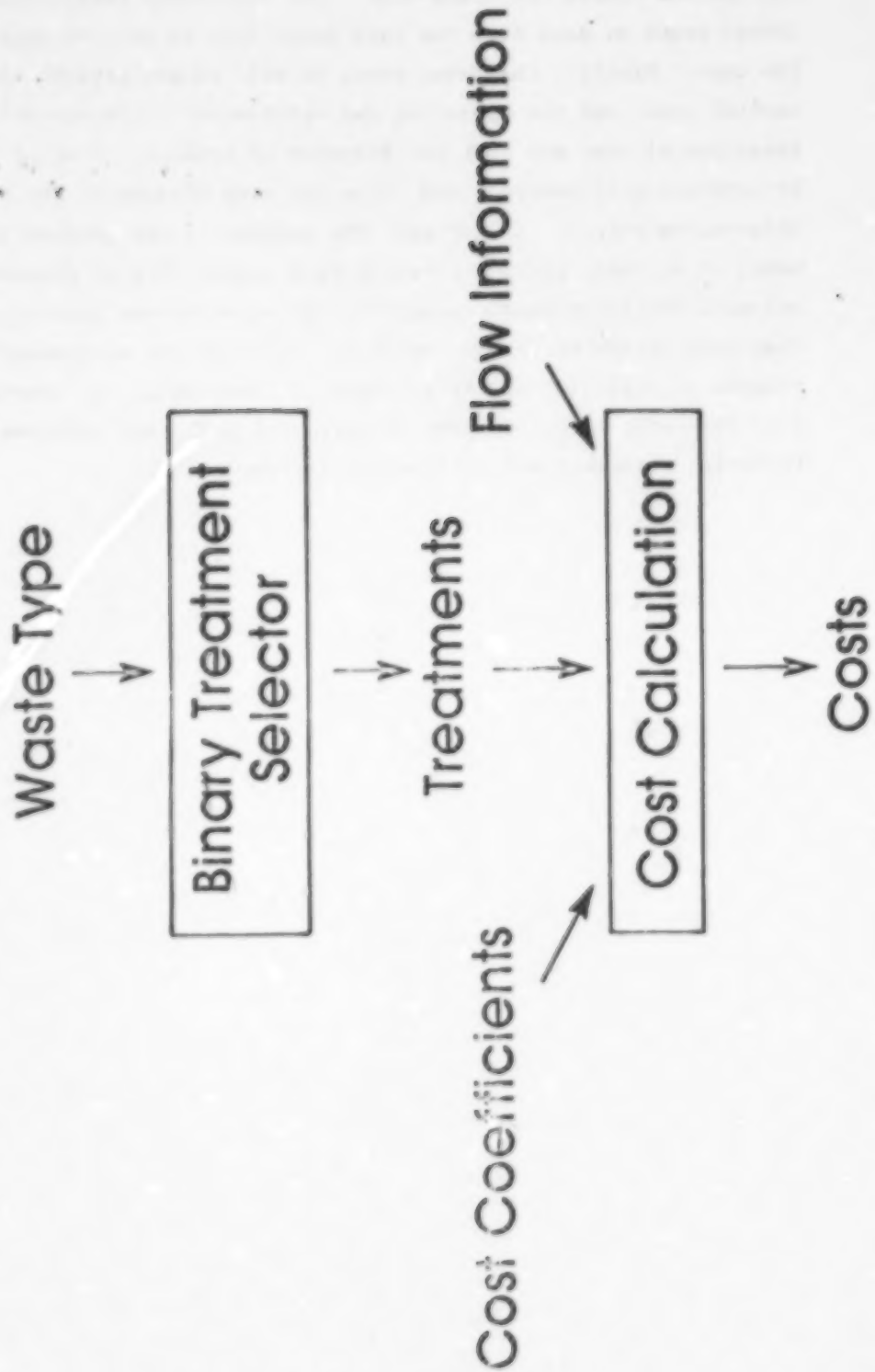


FIGURE 6

Program Schematic



the treatment options to be determined and displayed to the user. The user then has the option of choosing which one to have costed or whether to have all of the options costed for comparison. The treatments themselves are individually costed based on data from the data input file as well as information provided by the user. Finally, the total cost, as well as the capital cost, the amortized capital cost, and the operating and maintenance costs are printed out in terms of total annual cost and cost per kilogram of product. Some of this information can be suppressed, if desired, and there are many options in the program for specifying information output. In general, the purpose of the program is to provide a ready means of not only getting a usable cost number, but of dissecting the costs and allowing choices between capital-intensive treatment trains and O&M-intensive treatment trains to be made readily. Although the environmental cost assessment program is still in the early stages of development, we consider it a valuable tool for early identification of potential pollution problems and for guidance for pollution abatement and elimination strategies.

OPENING REMARKS BY GLENN PRATT
WORKSHOP COORDINATOR, U.S. EPA, REGION V
CONTINUATION OF WORKSHOP ON THE IDENTIFICATION, EVALUATION,
AND CONTROL OF TOXIC SUBSTANCES IN INDUSTRIAL EFFLUENTS

JUNE 16, 1982

GOOD MORNING. I AM VERY PLEASED TO WELCOME YOU TO DAY TWO OF OUR WORKSHOP ON THE IDENTIFICATION, EVALUATION AND CONTROL OF TOXIC SUBSTANCES IN INDUSTRIAL EFFLUENTS. THIS WORKSHOP IS BEING JOINTLY SPONSORED BY THE U.S. DEPARTMENT OF COMMERCE, THE ILLINOIS CHAMBER OF COMMERCE AND THE ILLINOIS INSTITUTE OF TECHNOLOGY - NOTRE DAME INDUSTRIAL WASTE ELIMINATION RESEARCH CENTER. AS VAL ADAMKUS STATED HERE YESTERDAY, THE PURPOSE OF THE WORKSHOP IS TO CONTINUE THE DIALOGUE BETWEEN INDUSTRY, ACADEMIA, AND THE REGULATORY COMMUNITY TO JOINTLY FOCUS ON THOSE POLLUTANTS THAT HAVE THE HIGHEST POTENTIAL FOR DAMAGE TO HUMAN HEALTH OR TO THE ENVIRONMENT.

CERTAINLY ONE OF THE MOST DIFFICULT TASKS FACING ALL OF US TODAY IS THE CONTINUED PROTECTION OF THE ENVIRONMENT WITHOUT AN UNREASONABLE LIMITATION OF INDUSTRIAL GROWTH AND DESPITE SHRINKING LOCAL, STATE, FEDERAL, AND INDUSTRIAL RESOURCES. CONTROLLING TOXIC CHEMICALS IN MUNICIPAL AND INDUSTRIAL WASTEWATERS IS AN IMPORTANT PART OF THIS TASK WHICH POSES A SIGNIFICANT CHALLENGE TO INDUSTRY AND TO THE POLLUTION CONTROL AGENCIES. WE ARE REMINDED THAT HUNDREDS OF NEW CHEMICALS ARE BEING PRODUCED ANNUALLY AND THAT MANY OF THESE CHEMICALS MAY FIND THEIR WAY INTO OUR LAKES AND STREAMS. THERE IS A CONTINUING NEED TO DEVELOP WAYS OF CONTROLLING TOXICANTS WHILE MAINTAINING THE ECONOMIC STRENGTH OF AMERICAN INDUSTRY.

FORTUNATELY, THERE ARE WAYS OF DEALING WITH THESE PROBLEMS, AND OUR "TOOLS" FOR DOING SO ARE IMPROVING. THESE ISSUES ARE BEING ADDRESSED HERE IN THIS TWO DAY WORKSHOP.

NATIONALLY, U.S. EPA IS DEVELOPING EFFLUENT GUIDELINES AND WATER QUALITY CRITERIA TO CONTROL THE DISCHARGE OF A SELECT NUMBER OF TOXICANTS OF NATIONAL CONCERN. IN ADDITION, U.S. EPA'S REGIONAL OFFICES, THE STATES, AND MUNICIPALITIES ARE NOW WORKING TO IMPLEMENT ECONOMICALLY VIABLE PROGRAMS TO ADDRESS FACILITIES WHICH MAY BE OF SPECIFIC LOCAL OR REGIONAL CONCERN BECAUSE OF THEIR PARTICULAR PRODUCTS, PROCESSES, RAW MATERIAL, ETC., OR TO ADDRESS THE UNIQUE ASSEMBLAGE OF INDUSTRIES IN A GIVEN RIVER OR LAKE BASIN. IN PARTICULAR, WE HAVE BEEN WORKING WITH THE STATES TO DEVELOP AND IMPLEMENT A TOXICANT CONTROL STRATEGY THAT FOCUSES ON THOSE FACILITIES WHICH HAVE THE HIGHEST POTENTIAL FOR THE DISCHARGE OF TOXICANTS WHICH MAY DAMAGE HUMAN HEALTH OR THE ENVIRONMENT.

THE WORKSHOP YESTERDAY AND TODAY IS INTENDED TO HELP INDUSTRY AND THE REGULATORY AGENCIES IDENTIFY POTENTIAL TOXICANTS WHICH MAY BE RELEASED TO THE ENVIRONMENT FROM A GIVEN MANUFACTURING PROCESS OR ACTIVITY, AND TO HELP EVALUATE WHICH OF THESE SUBSTANCES MAY BE OF CONCERN. THE WORKSHOP YESTERDAY WAS COORDINATED WITH DR. JAMES PATTERSON OF THE ILLINOIS INSTITUTE OF TECHNOLOGY - NOTRE DAME INDUSTRIAL WASTE ELIMINATION RESEARCH CENTER AND FOCUSED ON THE IDENTIFICATION OF TOXICANTS. THE WORKSHOP TODAY WILL FOCUS ON THE EVALUATION OF TOXICITY POTENTIAL AND WILL FEATURE THE USE OF TOOLS DEVELOPED BY THE PHARMACEUTICAL INDUSTRY, AS WELL AS U.S. EPA'S

EFFORTS IN THE FIELD OF CHEMICAL/ACTIVITY RELATIONSHIPS AND THEIR USE IN PREDICTING PERSISTENCE, BIOACCUMULATION, AQUATIC AND MAMMALIAN TOXICITY, CARCINOGENICITY, ETC. TODAY'S WORKSHOP HAS BEEN COORDINATED WITH THE AGENCY'S ENVIRONMENTAL RESEARCH LABORATORY IN DULUTH.

WE ARE HERE TODAY TO TRY TO JOINTLY LOOK AT WHAT MORE MAY NEED TO BE ACCOMPLISHED AND HOW WE CAN BOTH BEST FOCUS OUR LIMITED RESOURCES TO CONTROL THOSE TOXICANT PROBLEMS THAT HAVE THE HIGHEST POTENTIAL FOR DAMAGE TO HUMAN HEALTH AND/OR THE ENVIRONMENT. WE LOOK FORWARD TO A PRODUCTIVE MEETING WITH YOU TODAY AND BELIEVE WE MUST WORK TO JOINTLY LAY OUT A SCIENTIFICALLY, ENVIRONMENTALLY, AND ECONOMICALLY DEFENSIBLE TOXICANT EVALUATION/CONTROL PROGRAM. WE WANT TO HEAR FROM YOU AND WORK WITH YOU NOT ONLY FOR THESE TWO DAYS, BUT CONTINUING INTO THE FUTURE. IT IS OUR HOPE THAT YESTERDAY AND TODAY'S WORKSHOP WILL BE OF USE TO YOU IN YOUR POLLUTION CONTROL EFFORTS. WE HOPE YOU WILL BE LOOKING TODAY TO SEE HOW THIS INFORMATION WILL BE OF USE TO YOU.

THE IDENTIFICATION AND FATE OF SELECTED ORGANIC
COMPOUNDS IN THE LOWER FOX RIVER, WISCONSIN

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ABSTRACT

A study was undertaken to identify the use of chemicals by industries and municipalities within a specific aquatic environment - Wisconsin's Lower Fox River, which drains into Green Bay, Lake Michigan. The Lower Fox River was chosen as a study site for a number of reasons. Kilometer for kilometer, the Lower Fox River is one of the most densely developed industrial rivers in the United States. Also, in 1978 the Wisconsin Department of Natural Resources identified over 100 organic compounds in the water, wastewaters, sediments, and biota of the Lower Fox River; 20 of these compounds appear on the U.S. EPA's list of priority pollutants. After identification of heavily used chemicals through the chemical inventory, an analytical program focused on the environmental fate of specific acidic and base neutral organic compounds. A fate assessment of the following compounds is presented here: dehydroabiatic acid, pentachlorophenol and retene. Also, a materials balance study at an integrated pulp and paper mill was completed for dehydroabiatic acid and retene.

INTRODUCTION

Controlling pollution from toxic substances in the Great Lakes Basin is a major issue confronting scientists and water quality planners (Sonzogni and Swain 1980). An overview of the potentially toxic compounds entering the Great Lakes Basin from anthropogenic sources was presented earlier (Delfino 1979), and the identification of potentially

troublesome industrial and municipal chemical inputs into the Basin is now beginning. It is apparent that there is a need for rapid identification of potentially toxic inputs to help scientists better focus their analytical efforts.

One approach to solving this problem is to inventory the chemicals used and manufactured by industries and municipalities within the Basin (Sullivan and Delfino 1982). To determine the feasibility of this approach we examined the movement of chemicals within a specific aquatic environment, Wisconsin's Lower Fox River which flows into Green Bay, Lake Michigan (Figure 1). The Lower Fox River was chosen as a study site since it is heavily industrialized and is the major tributary to Green Bay, one of the most biologically productive and important ecosystems of Lake Michigan (Bertrand *et. al.*, 1976; Great Lakes Fishery Commission 1979).

The chemical inventory was designed to meet the following objectives.

- 1) Determine the worst potential case of toxic chemical discharge from point sources.
- 2) Serve as a companion approach to a field and laboratory analytical effort in the study area.
- 3) Use the inventory to provide a means of ascertaining the types of industrial chemicals that could be expected to occur in readily detectable amounts in the aquatic environment.

The chemical inventory is intended to be used by agency personnel and by other researchers in the following ways.

- 1) By identifying troublesome and potentially toxic compounds through the inventory, their pathways and fates may be assessed and proper regulations developed, if necessary, to ensure public safety and health.

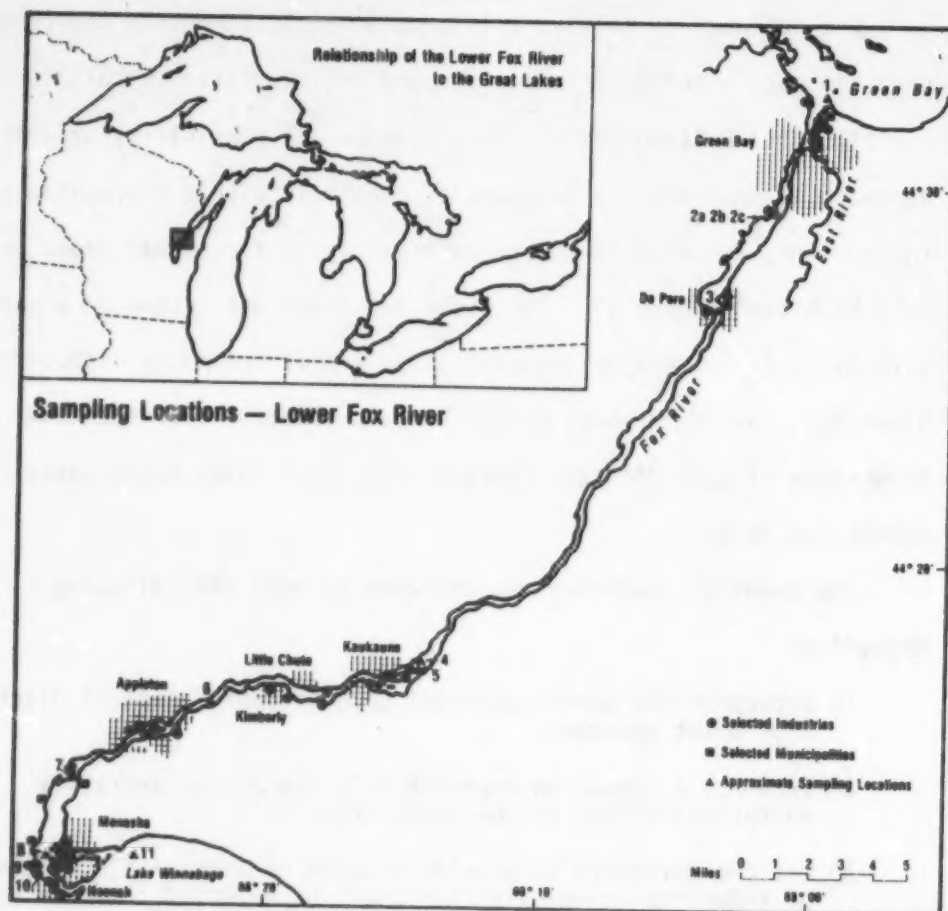


Figure 1. Selected industrial and municipal waste discharges to the Lower Fox River, with inset showing geographical location in the Great Lakes Basin.

- 2) Use the inventory to determine which raw chemicals may need to be replaced or removed by treatment if undesirable levels of certain compounds are present in an effluent.
- 3) Once a compound is identified within the aquatic environment, work back to the inventory to help explain the compound's existence in the ecosystem.

INFORMATION ACQUISITION

We took the following approach to complete the chemical inventory of the Lower Fox River Basin.

STATE LEVEL

At the state level we first contacted the Wisconsin Department of Natural Resources (WDNR). (Figure 2). The agency carries out the mandates of various federal and state laws. By reviewing the 208 Basin Plan, a requirement of PL 92-500, we identified all significant dischargers to the Lower Fox River. Simultaneously, we contacted the municipalities discharging to the river. From the municipalities, we requested and received lists of significant dischargers to their facilities as well as an inventory of chemicals used in treating their incoming wastes. Once a majority of the industries were identified, the WDNR files were reviewed for information regarding chemical usage and manufacture.

In our project, if the WDNR files did not provide the needed information for the inventory, a letter was sent to the industry requesting further details. The responses to these inquiries provided some useful additional information.

FEDERAL LEVEL

Along with the inventory data found at the state level, information sources at the federal level were explored (Figure 3). Section 308 of the 1977 Amendments to The Federal Water Pollution Control Act, commonly

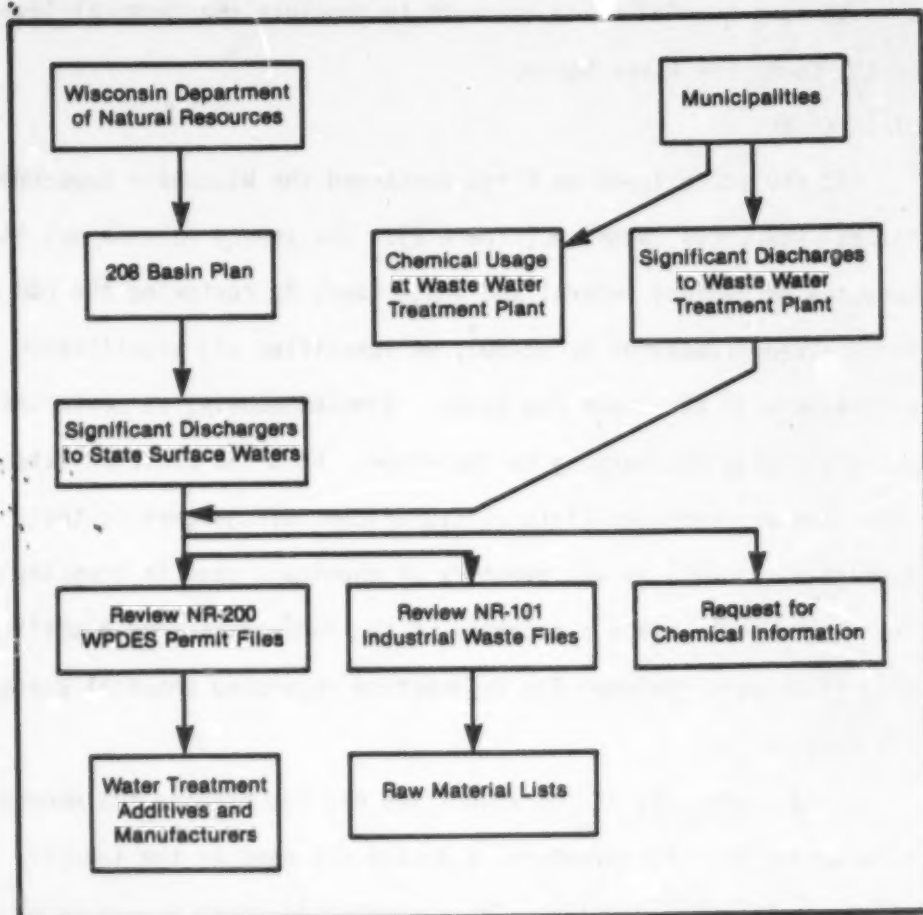


Figure 2. Information sources at the state level.

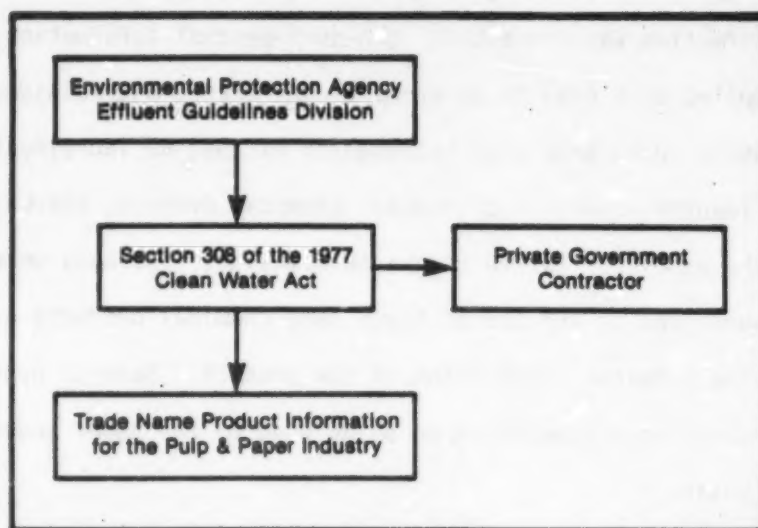


Figure 3. Information sources at the federal level.

called the Clean Water Act (PL 95-217), requires the reporting of chemicals used within certain industrial categories one of which is the "pulp and paper board mills and converted paper products industry." To obtain this information, the Effluent Guidelines Division of the United States Environmental Protection Agency (EPA) in Washington, D.C. was contacted. Since pulp and paper mills are the dominant industry in the Lower Fox River Basin, this was the industrial category for which chemical information was requested. Non-confidential information, which had been compiled by a private government contractor, was released to us. Confidential data were also released to us, but no individual company was identified with a particular chemical product, thereby preserving the anonymous nature of the information. The data were originally submitted to the EPA as trade name chemical products and did not contain the chemical composition of the product. Several hundred chemical products were identified as being used by the paper industry within this basin.

DEVELOPMENT OF THE INVENTORY

Much of the chemical information obtained from the various sources was too general to be put directly into the inventory to meet the objectives of the project. Therefore, we had to compile the chemical data from all sources and identify the chemical compositions of as many as possible of the trade name chemical products (Sullivan and Delfino 1982). Historically, there had not been any one reference or group of references available for identifying chemical compositions of many trade

name products. In fact, until recently, many chemical suppliers themselves were not sure of the exact chemical composition of their products. With the implementation of the Toxic Substances Control Act (TSCA, PL 94-469), which is administered by the EPA, we now have a detailed list of chemicals and/or trade names of products manufactured in, or imported into the United States. The list appears in the Toxic Substances Control Act Chemical Substance Inventory published in May, 1979. This four volume set, plus supplements, enables many trade name chemical products to be identified according to their exact chemical composition. This information, which will probably be periodically updated, is a key element in current and future efforts to identify and evaluate hazards associated with chemical substances already in commercial use. Future additions to the TSCA inventory will require, for the first time, that new chemical substances be assessed for potential problems before they are manufactured and possibly released to the environment.

In our project, we used the TSCA inventory to determine the chemical compositions of trade name products, although for the majority of trade name chemical products, only a manufacturer of the product(s) could be obtained (Sullivan and Delfino 1982). After we matched trade name products to manufacturers, letters were mailed to the companies requesting the chemical composition of the product(s) as well as material safety data sheets as required by PL 91-596, the Occupational Safety and Health Act of 1970. The amount and usefulness of the information provided to us varied from company to company.

Once the identification phase was completed, the information was compiled into a select inventory of chemicals manufactured and used within the Lower Fox River Basin (Sullivan and Delfino 1982). Any given entry in the inventory includes as many of the following items as were available: the trade name chemical product, chemical composition, Chemical Abstract Service (CAS) registry number, molecular formula, manufacturer(s), user(s), quantities and use of the product. Other information listed, where it was available, includes: aquatic toxicity data, chemical stability data, decomposition products and proper disposal procedures. A summary of the most highly used and/or manufactured organic chemicals, is given in Table 1.

LINKAGES BETWEEN THE CHEMICAL INVENTORY AND SELECTED ENVIRONMENTAL POLLUTANTS

Many studies have been performed to assess the extent of organic pollutants in industrial effluents, sediments, and biota in the Lower Fox River study area (Peterman et al., 1980; Veith et al., 1979; Buelow 1982 and Groose 1982). More than 100 organic compounds in river water, effluent, sediment and biota samples taken from the Lower Fox River were identified by Peterman et al. (1980). A number of these organic compounds can be traced to raw materials used in the study area and which appear in the chemical inventory (Sullivan and Delfino 1982).

For example, dehydroabiatic acid (DHA) and pentachlorophenol (PCP) are contained in raw materials used by industries in the Lower Fox River Basin (See Table 1). Dehydroabiatic acid, a resin acid, can reach the

Table 1. The most highly used/manufactured organic materials in the Lower Fox River Basin

Organic Materials	Amount (tons/yr)	Number Reporting*
Rosin Size ¹	2,900	(7 of 9)
Resins (Wet Strength)	2,800	(5 of 15)
Urea CAS #57-13-6 M.F. $\text{CH}_4\text{N}_2\text{O}$	1,727	(2 of 2)
Dyes ²	1,270	(8 of 20)
Ethene, homopolymer CAS #9002-88-4 M.F. $(\text{C}_2\text{H}_4)_x$	930	(1 of 4)
Ethanol, homopolymer CAS #9002-89-5 M.F. $(\text{C}_2\text{H}_4\text{O})_x$	237	(1 of 2)
Accosize 17 ³	114	(1 of 1)
Slimicides & Biocides ⁴	80	(5 of 20)
Hercofloc 815 ⁵	60	(1 of 1)
Versene CAS #60-00-4 M.F. $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$	37	(1 of 2)

*Number of industries reporting quantities out of the total number of industries reporting use of the material.

1) Typical ingredients: A mixture of resin acids, including dehydroabiatic acid.

2) Sum of many.

3) Active ingredients: Succinic anhydride

4) Typical ingredients: 2-(Thiocyanomethylthio) benzothiazole
3,5-dimethyl-1,3,5, 2H tetrahydrothiadiazine-2-thione
Pentachlorophenol, sodium salt
2,4,5-Trichlorophenol, sodium salt

5) Acrylamide based copolymer.

Lower Fox River aquatic environment via two major sources. Resin acids occur naturally in wood and are released to the aquatic environment through the pulping of wood. Also, DHA is a major component of rosin size which is a raw material added as a sizing agent in the making of paper. DHA is toxic to fish at around 1 mg/L (Leach and Thakore, 1977), it is persistent in water and sediments (Fox, 1977; Brownlee and Strachan 1976), it bioaccumulates in fish (Fox *et al.*, 1977), is chlorinated in the bleaching of pulp (Thakore and Oehlshlager, 1977), and is Ames test mutagenic (Kinae *et al.*, 1981).

Pentachlorophenol in the past and still to some extent today is used as a slimicide in the process and cooling water streams of paper mills. Pentachlorophenol is on the EPA priority pollutant list and the EPA has proposed effluent limitations for them. (Pulp and Paper Point Sources Task Force 1981). Pentachlorophenol is apparently not formed during the pulp bleaching process (Claeys *et al.*, 1980; Pulp and Paper Point Sources Task Force 1981). Therefore, if pentachlorophenol is found in a discharge, it is likely there as an additive or is a contaminant in other raw materials used in a paper mill process or cooling water stream. The major degradation products of pentachlorophenol include two isomers of tetrachlorophenol (TCP) and pentachloroanisole (Pierce and Victor 1978). Apparently, photodegradation accounts for the formation of the two TCP isomers while pentachloroanisole may be formed by bacteria in the sediment of the aquatic ecosystem (Veith *et al.*, 1981).

Recent analyses of fish tissue from our study area showed pentachloroanisole to be present in some of the fish species (Wisconsin State Laboratory of Hygiene, 1982). Pentachlorophenol is potentially

toxic to fish with 96 hr LC_{50} ranges of 0.037 to 0.130 mg/L for Salmonids (Davis and Hoos 1975) and its degradation products and possibly some raw material contaminants may also be toxic (Pierce and Victor 1978). This information coupled with the known fish flesh tainting tendencies of chlorophenols (Federal Register 1980, Pulp and Paper Task Force 1981) points to the need to minimize the discharge of these compounds to protect the fishery.

Retene (1-methyl,7-isopropyl phenanthrene) is one of several diterpene hydrocarbons which was identified in the GC-MS screening of sediments of the Lower Fox River for neutral organic compounds (Buelow, 1982). The toxicity of retene in the aquatic environment is unknown. Although, its route of entry into the aquatic environment is better understood. It has been suggested by LaFlamme and Hites (1978) as the end product of the degradation of dehydroabietic or abietic acid.

Although several diterpene hydrocarbons, such as abietadiene, pimaradiene, and dehydroabietane are wood extractives (Joye *et al.*, 1973; Lu *et al.*, 1975; Conner *et al.*, 1980), retene is not known as a plant product (Eglinton 1968). Skrigan (1964) found evidence for the hydrogenation and dehydrogenation of abietic acid to fichtellite and retene, respectively, in a fossilized pine stump.

Retene and related diterpene hydrocarbons have also been identified in unburned coal (Hayatsu *et al.*, 1978; White and Lee, 1980; Shaw and Wiggs, 1980), in sediments (Simoneit, 1977a and 1977b; Simoneit *et al.*, 1979; Wakeham *et al.*, 1980; Tan and Heit, 1981), and in soils (LaFlamme and Hites, 1978; Wakeham *et al.*, 1980). Yamaoka (1979 and 1981) and Kinae *et al.* (1981) detected retene in marine sediments impacted by discharges from pulp and paper mills.

LaFlamme and Hites (1978) and Wakeham *et al.*, (1980) presented degradation schemes in which abietic acid is converted to retene by pathways such as that given in Figure 4, to explain the presence of retene and several of the intermediates in sediments and in conifer forest soils. Although this degradation pathway is hypothetical, the dehydrogenation of abietic acid to retene in the laboratory by heating with sulfur or selenium is well known (Fieser and Fieser 1949).

ANALYTICAL TECHNIQUES

Water and wastewater samples were liquid-liquid extracted into base/neutral and acid extractable fractions. Soxhlet extraction followed by liquid-liquid back extraction yielded base/neutral and acid fractions from sediments and sludges. Retene and diterpenoid hydrocarbons were isolated from the base/neutral fractions by column chromatography on Florisil and silica gel. The acid fraction containing dehydroabietic acid and pentachlorophenol was methylated prior to gas chromatographic analysis. Complete details of the analytical scheme are given elsewhere (Buelow 1982; Goose 1982).

QUALITATIVE ASSESSMENT OF DHA, PCP AND RETENE IN THE AQUATIC ENVIRONMENT

The presence of DHA in the water and sediments of the Lower Fox River is nearly universal. All sediment samples, except one, contained DHA. The highest concentration found in the Lower Fox River was below a deink-fine and tissue paper mill (See Table 2). This is lower than the highest concentration found in sediments below a kraft pulp and paper mill on Lake Superior (150 mg/kg, Brownlee *et al.*, 1977).

Dehydroabietic acid has been found to be biodegradable, especially in

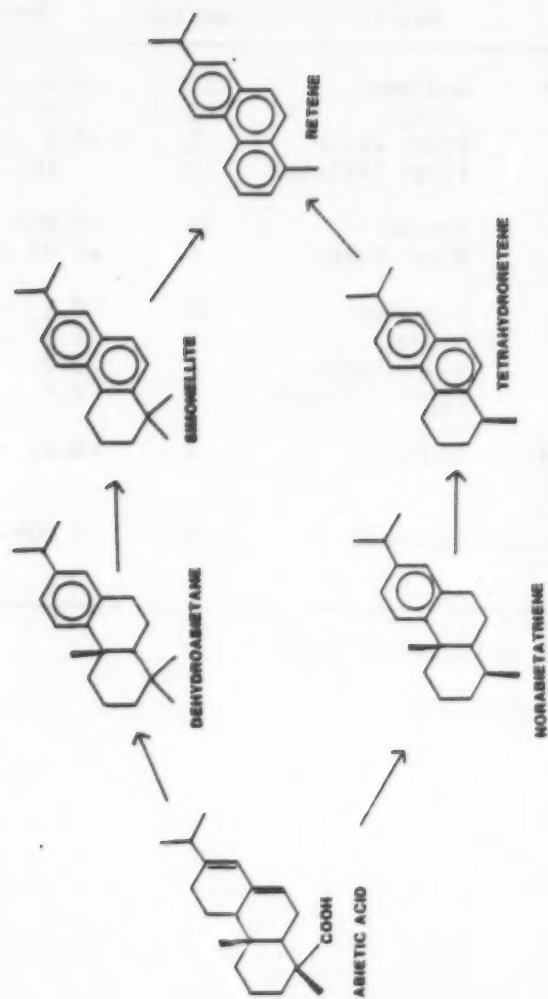


Figure 4. Biogenic formation of retene.

Table 2. Compounds Identified and Quantified in Samples from the Lower Fox River System.

Compound	Sample Matrix	Number of Samples	Concentration Range	Units
Dehydroabiatic Acid	Sediment	15	<0.05 - 26	mg/kg*
	Sludge	3	290 - 480	mg/kg*
	River Water	5	<0.2 - 36	µg/L
	Final Effluent	2	16 - 140	µg/L
Pentachlorophenol	Sediment	15	<0.005- 1.2	mg/kg*
	River Water	5	<0.02 - 1.0	µg/L
Retene	Sediment	15	0.1 - 26.0	mg/kg*
	Sludge	3	6.8 - 17.8	mg/kg*
	River Water	5	<0.2	µg/L
	Final Effluent	2	2.7	µg/L
Chlorodehydroabiatic Acid (2 isomers)	Sediment	6	<0.01 - 4	mg/kg*
Dichlorodehydroabiatic Acid	Sediment	6	<0.005- 5	mg/kg*

*dry weight basis
(from Goose, 1982 and Buelow, 1982)

acclimated wastewater treatment systems (Mueller *et al.*, 1977; Leach *et al.*, 1978). A disappearance half-life of 21 years in sediments and 0.12 years in the water column and surface sediments were determined for DHA in Nipigon Bay of Lake Superior (Brownlee *et al.*, 1977). The background concentration of DHA in the Lower Fox River water was around 2 ug/L while the highest concentrations were found in pulp and paper mill effluent plumes before complete dilution with the Lower Fox River (See Table 2).

Pentachlorophenol was detected in one location in the Lower Fox River waters, in the effluent plume of a deink-fine and tissue paper mill (1.00 ug/L). While most mills no longer use PCP as a slimicide, apparently at least one mill still uses it. The sediment of the Lower Fox River has accumulated PCP as high as 1.23 mg/kg dry sediment. This concentration may persist for a long period of time because of slow degradation of PCP.

Retene was detected in a pulp and paper mill final effluent at approximately 3 ug/L, but was not detected in river water surface samples, presumably due to the dilution factor. Concentrations in several sediment samples ranged from approximately 0.1 mg/kg to 26 mg/kg, with nine of the fifteen sampling sites having concentrations greater than 1 mg/kg (See Table 2).

DHA AND RETENE MASS BALANCE IN A PULP AND PAPER MILL

A limited mass balance of DHA and retene was performed in one integrated unbleached pulp and paper mill (See Figure 5). Process intake water from the Lower Fox River, pulp and paper mill untreated

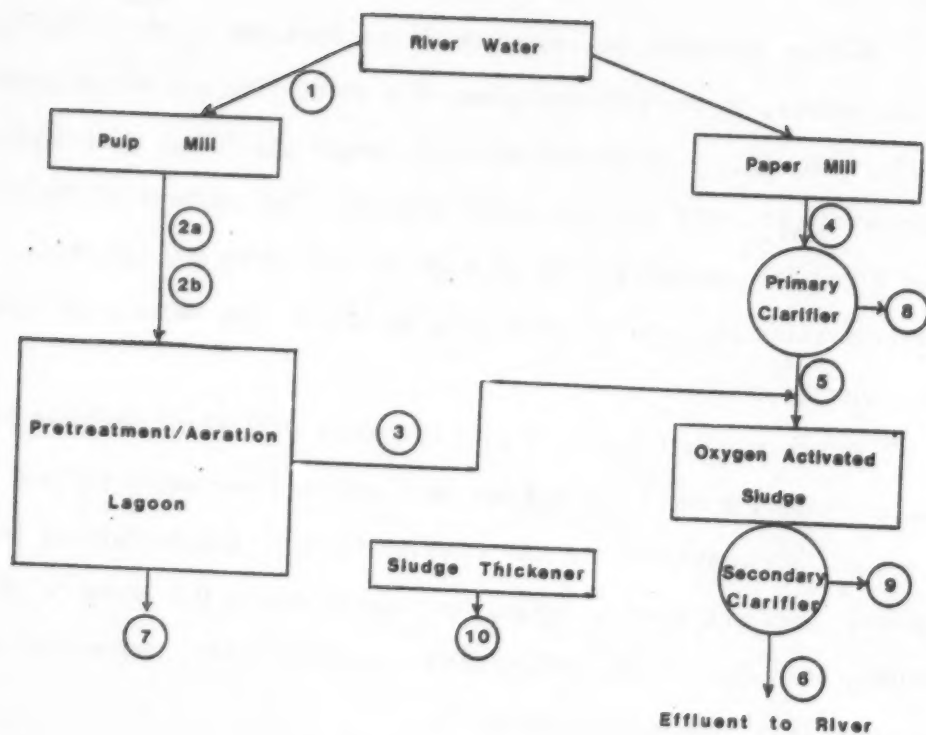


Figure 5. Wastewater treatment system schematic for an integrated kraft unbleached pulp and paper mill. Numbers indicate sampling sites.

wastewaters, two samples within the treatment system, and the final effluent were all monitored for DHA and retene. The concentration for DHA in the intake water was 2 ug/L, pulp mill effluent 310 ug/L, paper mill effluent 1840 ug/L, with a reduction to 130 ug/L in the final effluent after biological treatment in a UNOX activated sludge system. A total system reduction of about 92% for DHA was determined (Groose, 1982).

The high levels in pulp mill effluent reflect DHA contribution to the wastewater stream as a natural extractive of wood. The paper mill effluent DHA concentration probably reflects the use of rosin size. Reported usage of dark rosin size was over 3500 L/day with a concentration of DHA greater than 1 g/L (Groose 1982). Only a minor amount of the DHA reduction was accounted for in the thickened sludge that was taken to landfill (Groose, 1982). Similar results were found in three mills investigated by Wallin and Condren (1981) where 0.02 to 5.4% of the DHA mass balance was accounted for in the sludge. Up to 50% of the DHA removed through the treatment system was accounted for with recycles of activated sludge to primary and secondary clarifiers. The remaining removal was probably because of biochemical degradation during biological treatment (Wallin and Condren 1981).

In the pulp and paper mill wastewater treatment system, retene was found at a concentration of 0.7 ug/L in raw effluents, and was not detected in rosin size. However, retene concentration in the effluent from the pulp mill aeration lagoon was 31 ug/L, which is 44 times higher than the concentration coming into the lagoon, indicating generation of retene in the aeration lagoon. Removal of retene through the UNOX and secondary clarifier was only 24%, on a g/day loading basis. Of the

total retene concentration in wastewaters, 50 to 75% was found on the particulates, indicating the sediments as the probable sink for retene in the aquatic system.

CONCLUSIONS AND NEEDED RESEARCH

The Lower Fox River has been the study site for numerous researchers. The identification and fate of many compounds as well as their main sources can now be explained. Yet, much work remains to be done to fully understand the sediments and biota of this river system. Questions remain as to why the sediments are largely devoid of life or why the fish seem to have an off flavor.

Future research activities that should be performed to help understand this aquatic environment and others include:

- 1) sorting the chemicals by known structure/activity relationships.
- 2) performing acute and chronic toxicity assays on heavily used chemicals that haven't been tested yet.
- 3) correlating chemical use with occurrence in plant process wastewaters and final effluent discharges;
- 4) performing mass balance studies within plants to determine the fate of heavily used chemicals; and
- 5) continuing to monitor biota, particularly fish, in the Lower Fox River for bioaccumulation of process chemicals and/or reaction products resulting from various in-plant activities.

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Estimation of Probability of Biodegradation of Chemicals

by

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This paper is a summary report on the structure-activity study reported in NTIS Report #PB82-100843. The report was authored by J. Geating, and the work was sponsored by the Franklin Research Institute, but the structure-activity research was apparently done entirely by an outside contractor and simply written up at Franklin. In the following summary of this work I will briefly discuss the data base used, the statistical analysis of the data, and finally the conclusions.

The objective of this piece of research was to see if a relation could be found between biodegradability and some set of structural descriptors. Data were assembled by searching the original literature for determinations of biodegradability. A compound was considered degradable if 10% or more of it degraded in a standard 10 day test; if less than 5% degraded it was considered non-degradable. In addition to these two reasonably well defined classes, there were a number of compounds for which the data were too ambiguous to make a choice between these two classes. The final data base contained approximately 700 compounds. Of these 60 were non-degradable, 600 were degradable, and 75 fell in the indeterminate category. To obtain a final data base the 600 degradable compounds were randomly sampled to give a sample of 296 degradables, which were combined with the other two categories to give a final data sample of approximately 430 compounds.

The structural descriptors chosen for this study were Wiswesser Line Notation codes (WLN). Wiswesser Line Notation is a compact form of code

which uses letters, symbols and numbers to represent complex chemical structures. It is not widely used but it is suitable for many computer problems in structural representation. About 250 functional groups were identified and their WLN were coded into the data base for each compound in which they appeared. A statistical analysis was then done to determine which of these keys could be used to construct a model for biodegradability in terms of structure as represented by these keys. The details of the statistical procedures are technical and will not be discussed here.

Several different equations or models were derived, but only one of these will be described. This final model included 39 of the structural keys, and was based entirely on the degradable and non-degradable segments of the data base. The indeterminate group of compounds were not included in this final study, and their behavior could not be predicted from it. They were omitted because it was found that they caused a great deal of "noise" in the statistical procedure. In lay terms, this means that inclusion of these compounds in the statistical calculations led to worse predictions for the well defined groups than were obtained when they were omitted.

The final result of this study was two equations, one to calculate a probability for degradability and the other to calculate non-degradability. Degradability can be predicted rather well by this equation. Of the 296 degradable compounds used in the study 270 were predicted to be degradable using the equation. There were 9 false predictions of degradability. This includes all compounds for which the probability of degradability was 0.7 or higher. Of the 61 non-degradable compounds 38 had a probability of degradability less than 0.1, and 4 of

the degradable compounds fell in this range. In the intermediate region between these two probability limits (0.7 - 0.3) there were 28 compounds; of these 28, 14 were incorrectly predicted if 0.5 was chosen as the logical dividing line between the two classes. The apparent difference in predictability is at least partly due to the difference in numbers of degradable and non-degradable compounds, but this bias may not be easy to remove from the data.

This study is interesting because it is the first attempt to carry out such a calculation for a very heterogeneous data base. Similar studies have been done on systems of compounds with some kind of structural relationship to each other. Examples of such classes are straight chain alcohols, 1,2-diols, or alpha-aminocarboxylic acids. This data base contained a much wider variety of compounds. However, no attempt has been made to explore possible bias in the data, except for the problem of the small number of cases in the non-degradable category.

ESTIMATING BIOCONCENTRATION
POTENTIAL FROM OCTANOL/WATER
PARTITION COEFFICIENTS

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Veith et al. [1] presented a structure-activity relationship for estimating the bioconcentration potential of chemicals in fish from the n-octanol/water partition coefficient (P or K_{ow}) which can be measured or computed from structure. The relationship was based on more than 50 tests from five general classes of chemicals and summarized as follows:

$$\log BCF = 0.85 \log P - 0.70 \quad R^2 = 0.897$$

The dependance of bioconcentration on the partition coefficient is comparable to many other SARs involving transport through biological membranes. Although the coefficient of 0.85 is commonly observed, it is only an empirically derived value resulting from the linear regression model imposed.

Mackay [2] derived a mechanistic relationship between bioconcentration and the partition coefficient in which the slope is 1.0 rather than 0.85. This linear model applied to the data of Veith et al. [1] resulted in the SAR

$$K_B = 0.048 K_{OW} \quad R^2 = 0.95$$

where K_B is the bioconcentration factor. This relationship yields a standard error of 0.25 in $\log K_B$ which is approximately a factor of two in K_B . This is adequate to screen chemicals to identify potentially bioaccumulative chemicals from those which do not produce residues and to provide an order of magnitude estimation of the bioaccumulation factor of chemicals under test conditions.

Although present funding does not permit continued testing of chemicals specifically from determination of bioconcentration factors, an on-going literature review has been conducted since 1979 to provide additional data for the model. Moreover, residues have been determined at the termination of 30-day embryo-larval toxicity tests being conducted at the Environmental Research Laboratory-Duluth. In these tests, the bioconcentration factor is simply the slope of the least-squares fit of residues in fish versus test concentration in the water. Only no-effect concentrations in these toxicity tests were used in determining the 30-day bioconcentration factors.

Bioconcentration factors and $\log P$ values for 122 bioaccumulation tests are presented in Table 1. The SAR was evaluated by regression analysis using different classes of chemicals and species of fish. The slope, intercept, number of data points, and R^2 for seven sets of data are summarized in Table 2. When only fathead minnow data on non-ionic chlorinated hydrocarbons were considered, the regression equation changed only slightly from Veith et al. [1] and R^2 increased from 0.90 to 0.92. Including only fathead minnow data on all classes of chemicals (54 tests), the SAR was indistinguishable from the Veith SAR. By including bluegill with fathead minnow data, the 88 tests lowered the slope from 0.85 to 0.81 and increased the intercept from -0.70 to -0.49. Adding the 9 tests with guppies did not alter the equation. Finally, examining the data of all 13 species of freshwater and marine fish and all classes of chemicals, the relationship between $\log BCF$ and $\log P$ is summarized as:

$$\log BCF = 0.79 \log P - 0.40 \quad N = 122 \quad R^2 = 0.86$$

The increase of the intercept from -0.70 to -0.40 is the only significant change in expanding the data base to 122 tests. This increase is associated with decrease in slope to 0.85 to 0.79 which means the predicted results are quite similar. In fact, the predicted BCF for a chemical with $\log$

$P = 5.00$ is 3548.1 by both the original equation with 59 tests and the expanded set of 122 tests.

If the linear model proposed by Mackay [2] were fitted to this data, the coefficient would be increased from 0.048 to 0.183 ± 0.389 .

On final result of this continuing evolution of the structure-bioaccumulation relationship is that the prediction limits of the regression did not significantly decrease by more than doubling the number of data points. Figures 1-3 present plots of the log BCF vs log P data smallest and most similar data set, the data set for only one species of fish, and, the entire set of all species and all chemicals. The dashed lines are the 95 percent prediction limits (the 95 percent confidence limit is extremely narrow) and it is quite apparent that the order of magnitude limit remains in all sets. This analysis suggests that the predictability is limited by the variance in the measured values themselves and/or the model and will not likely be improved by generating new data with similar inherent errors. Although it must be emphasized that the SAR (with order of magnitude accuracy) can only be used to screen chemicals, the data do show that the single SAR is useful for a wide variety of species and a wide range of chemical properties.

The structure-bioaccumulation relationship has one limitation which has not been thoroughly investigated. The equation implies that the bioconcentration factor will increase without bounds as log P increases. However, increases in log P is often accompanied by an increase in molecular volume which eventually is sufficiently large to inhibit membrane permeability. Polychlorinated paraffins (Chlorafin[®] etc.) have molecular weights in excess of 700 and do not appear to bioconcentrate in fish. We have also tested hexabromobenzene in a conventional 28-day test with no evidence of residues in fish other than what would be expected from simple adsorption on the surface of the fish. Consequently, there is evidence of a steric cutoff however undefined at this time. A rule-of-thumb discussed by several investigators is that the log BCF/log P relationship should be used with caution for chemicals with a molecular weight greater than 600.

Table I. Summary of Bioconcentration Factors for Chemicals in Fish

Chemical	Ref	Log P	Log BCF	Species	Time	Tissue
Lindane	1	3.85	2.67	Fathead	304D	W. body
Atrazine	1	2.63	0.90	Fathead	276D	W. body
Heptachlor	1	5.44	4.30	Fathead	276D	W. body
2-Ethylhexaphthalate	1	4.20	2.93	Fathead	56D	W. body
DASC-3	1	1.00	0.32	Bluegill	30D	W. body
DASC-4	1	1.00	0.32	Bluegill	30D	W. body
NTS-1	1	1.00	0.66	Bluegill	35D	W. body
BSB	1	1.00	0.32	Bluegill	50D	W. body
FWA-2-A	1	1.80	0.32	Bluegill	105D	W. body
FWA-3-A	1	1.48	0.32	Bluegill	105D	W. body
FWA-4-A	1	1.20	0.32	Bluegill	105D	W. body
Nitrobenzene	1	2.93	1.18	Fathead	28D	W. body
P-Nitrophenol	1	1.91	1.88	Fathead	28D	W. body
Naphthalene	1	3.59	2.63	Fathead	28D	W. body
Chlorobenzene	1	3.79	2.65	Fathead	28D	W. body
2,4,5-Trichlorophenol	1	3.72	3.28	Fathead	28D	W. body
Endrin	1	4.56	3.66	Fathead	300D	W. body
1,1,2,2-Tetrachloroethylene	1	2.88	2.06	Rainbow Trout	4D	Muscle
Hexachlorobenzene	1	6.18	4.37	Rainbow Trout	4D	Muscle
P-Biphenylphenyl Ether	1	5.55	3.22	Rainbow Trout	4D	Muscle
Diphenyl Ether	1	4.21	2.77	Rainbow Trout	4D	Muscle
Carbon Tetrachloride	1	2.64	1.72	Rainbow Trout	4D	Muscle
P-Dichlorobenzene	1	3.38	2.81	Rainbow Trout	4D	Muscle
Biphenyl	1	4.09	3.12	Rainbow Trout	4D	Muscle

Table I (Continued)

Chemical	Ref	Log P	Log BCF	Species	Time	Tissue
Chloropyrifos	1	4.82	2.67	Mosquito Fish	35D	W. body
Endrin	1	4.56	3.17	Mosquito Fish	35D	W. body
2,5,6-Trichloropyridinol	1	1.35	0.49	Mosquito Fish	35D	W. body
Fluorene	1	4.38	3.11	Fathead	28D	W. body
Dibenzofuran	1	4.12	3.13	Fathead	28D	W. body
2-Chlorophenanthrene	1	5.16	3.63	Fathead	28D	W. body
Phenanthrene	1	4.46	3.42	Fathead	4D	W. body
2-Methylphenanthrene	1	4.86	3.48	Fathead	4D	W. body
Heptachlor	1	5.44	3.98	Fathead	32D	W. body
Heptachloroepoxide	1	5.40	4.16	Fathead	32D	W. body
P,P'-DDE	1	5.69	4.71	Fathead	32D	W. body
Pentachlorophenol	1	2.97	2.89	Fathead	32D	W. body
Hexabromobiphenyl	1	6.39	4.26	Fathead	32D	W. body
Methoxychlor	1	4.30	3.92	Fathead	32D	W. body
Mirex	1	6.89	4.26	Fathead	32D	W. body
Hexabromocyclododecane	1	5.81	4.26	Fathead	32D	W. body
Heptachloronorbornene	1	5.28	4.05	Fathead	32D	W. body
Hexachloronorbornadiene	1	5.28	3.81	Fathead	32D	W. body
1,2-Dichlorobenzene	8	3.40	1.95	Bluegill	14D	W. body
1,3-Dichlorobenzene	8	3.44	1.82	Bluegill	14D	W. body
1,4-Dichlorobenzene	8	3.37	1.78	Bluegill	14D	W. body
1,2,3,5-Tetrachlorobenzene	8	4.46	3.26	Bluegill	28D	W. body
Pentachlorobenzene	8	4.94	3.53	Bluegill	28D	W. body
Carbon Tetrachloride	8	2.73	1.48	Bluegill	21D	W. body

Table I (Continued)

Chemical	Ref	Log P	Log BCF	Species	Time	Tissue
Chloroform	8	1.90	0.78	Bluegill	14D	W. body
1,2-Dichloroethane	8	1.45	0.30	Bluegill	14D	W. body
1,1,1-Trichloroethane	8	2.47	0.95	Bluegill	20D	W. body
1,1,2,2-Tetrachloroethane	8	2.39	0.90	Bluegill	14D	W. body
Pentachloroethane	8	3.21	1.83	Bluegill	14D	W. body
Hexachloroethane	8	3.93	2.14	Bluegill	28D	W. body
Bis(2-Chloroethyl)Ether	8	1.12	1.04	Bluegill	14D	W. body
1,1,2-Trichloroethylene	8	2.42	1.23	Bluegill	14D	W. body
Tetrachloroethylene	8	2.53	1.69	Bluegill	21D	W. body
Isophorone	8	1.67	0.84	Bluegill	14D	W. body
N-Nitrosophenylamine	8	3.13	2.34	Bluegill	14D	W. body
2-Chlorophenol	8	2.16	2.33	Bluegill	28D	W. body
2,4-Dimethylphenol	8	2.16	2.33	Bluegill	28D	W. body
Butylbenzylphthalate	8	4.05	2.89	Bluegill	21D	W. body
Dimethylphthalate	8	1.61	1.76	Bluegill	21D	W. body
Diethylphthalate	8	2.70	2.07	Bluegill	21D	W. body
Alkyl Benzene Sulfonate	9	1.59	2.02	Bluegill	21D	W. body
Alkyl Benzene Sulfonate	9	1.59	1.56	Bluegill	21D	Muscle
Naphthalene	17	3.59	1.90	Coho Salmon	35D	Muscle
2-Methylnaphthalene	17	3.84	2.28	Coho Salmon	35D	Muscle
1-Methylnaphthalene	17	3.84	2.11	Coho Salmon	35D	Muscle
Hexachlorocyclohexane	11	3.85	2.15	Guppy	4D	W. body
Hexachlorocyclohexane	12	3.85	2.70	Guppy	4D	W. body
Endrin	13	4.56	4.02	Flagfish	30D	W. body

Table I (Continued)

Chemical	Ref	Log P	Log BCF	Species	Time	Tissue
Tricresyl-Phosphate	1	3.42	2.22	Fathead	32D	W. body
Diphenyl Amine	1	3.42	1.48	Fathead	32D	W. body
Toluene	1	3.16	1.96	Fathead	32D	W. body
Tetrachloroethylene	2	2.53	1.79	Fathead	30D	W. body
1,1,2,2-Tetrachloroethane	2	2.39	0.91	Fathead	30D	W. body
Pentachloroethane	2	3.21	1.78	Fathead	30D	W. body
Hexachloroethane	2	3.93	2.85	Fathead	30D	W. body
1,3-Dichlorobenzene	2	3.44	1.99	Fathead	30D	W. body
1,4-Dichlorobenzene	2	3.37	2.05	Fathead	30D	W. body
1,2,4-Trichlorobenzene	2	4.52	2.60	Fathead	30D	W. body
1,2,3,4-Tetrachlorobenzene	2	4.46	3.41	Fathead	30D	W. body
Hexachlorobenzene	2	6.18	4.37	Fathead	30D	W. body
Hexachloro 1,3-Butadiene	2	5.10	3.84	Fathead	30D	W. body
Acridine	3	3.30	2.10	Fathead	17D	W. body
Toxaphene	4	5.28	3.64	Sheepshead Minnow	4D	W. body
Toxaphene	4	5.28	3.59	Pinfish	4D	W. body
Pentachlorophenol	10	2.97	1.11	Bluegill	8D	Muscle
Imidan	5	2.83	0.90	Fathead	2D	W. body
Imidan	5	2.83	1.04	Channel Catfish	2D	W. body
Imidan	5	2.83	0.90	Bluegill	2D	W. body
Diazinon	6	1.92	2.18	Topmouth Gudgeon	7D	W. body
Diazinon	6	1.92	1.56	Silver Crucian Car	7D	W. body
Diazinon	6	1.92	1.81	Carp	7D	W. body
Diazinon	6	1.92	1.24	Guppy	7D	W. body

Table I (Continued)

Chemical	Ref	Log P	Log BCF	Species	Time	Tissue
Endrin	13	4.56	4.18	Flagfish	65D	W. body
Endrin	13	4.56	3.85	Flagfish	110D	W. body
Al254	14	6.47	4.60	Brook Trout	118D	W. body
Al254	15	6.47	4.43	Spot	56D	W. body
1,4-Dichlorobenzene	16	3.37	1.96	Guppy	19D	W. body
1,2,3-Trichlorobenzene	16	4.20	2.81	Guppy	19D	W. body
1,3,5-Trichlorobenzene	16	4.20	2.85	Guppy	19D	W. body
1,2,3,5-Tetrachlorobenzene	16	4.46	3.56	Guppy	19D	W. body
Pentachlorobenzene	16	4.94	4.11	Guppy	19D	W. body
Hexachlorobenzene	16	6.18	4.16	Guppy	19D	W. body
Aroclor 1016	1	5.88	4.63	Fathead	32D	W. body
Aroclor 1248	1	6.11	4.85	Fathead	32D	W. body
Aroclor 1254	1	6.47	5.00	Fathead	32D	W. body
Aroclor 1260	1	6.91	5.29	Fathead	32D	W. body
Chlorodane	1	6.00	4.58	Fathead	32D	W. body
Octachlorostyrene	1	6.29	4.52	Fathead	32D	W. body
P,P-DDT	1	5.75	4.47	Fathead	32D	W. body
O,P'-DDT	1	5.75	4.57	Fathead	32D	W. body
Hexachlorobenzene	1	6.18	4.27	Fathead	32D	W. body
1,2,4-Trichlorobenzene	1	4.23	3.32	Fathead	32D	W. body
Lindane	1	3.85	2.26	Fathead	32D	W. body
5-Bromoindole	1	2.97	1.15	Fathead	32D	W. body
2,4,6-Tribromoisol	1	4.48	2.94	Fathead	32D	W. body
N-Phenyl-2-Naphylamine	1	4.38	2.17	Fathead	32D	W. body

Table I (Continued)

Chemical	Ref	Log P	Log BCF	Species	Time	Tissue
Endrin Acenaphthene	7	4.56	3.21	Channel Catfish	55D	W. body
	8	3.92	2.59	Bluegill	28D	W. body

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Table I (Continued)

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Table II. Regression Analysis of Bioconcentration Data Sets: $\text{Log BCF} = a \text{ Log P} + b$

Data Set	Slope (a)	Intercept (b)	N	R ²
Veith et al. (1979) mixed species	0.85	-0.70	59	0.90
Fathead minnow, non-ionic chlorinated hydrocarbons	0.86	-0.80	16	0.92
All fathead minnow data > 20 day exposure	0.85	-0.63	50	0.86
All fathead minnow data	0.86	-0.72	54	0.86
All fathead minnow and bluegill data	0.81	-0.49	88	0.87
All fathead minnow, bluegill, guppy data	0.81	-0.49	97	0.87
All species, all chemicals	0.79	-0.40	122	0.86

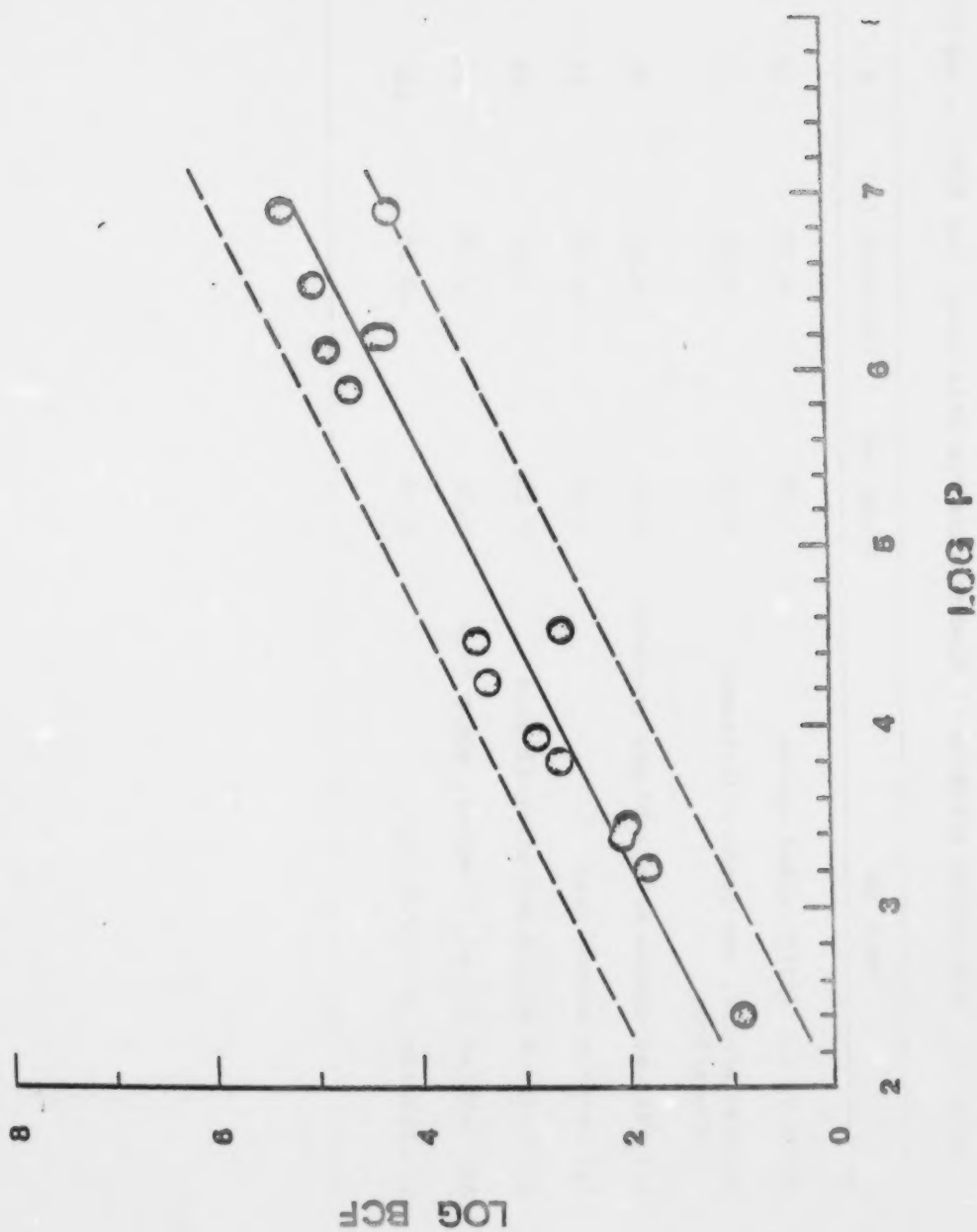


Figure 1. Relationship between log P and log BCF for nonionic chlorinated hydrocarbons and fathead minnows.

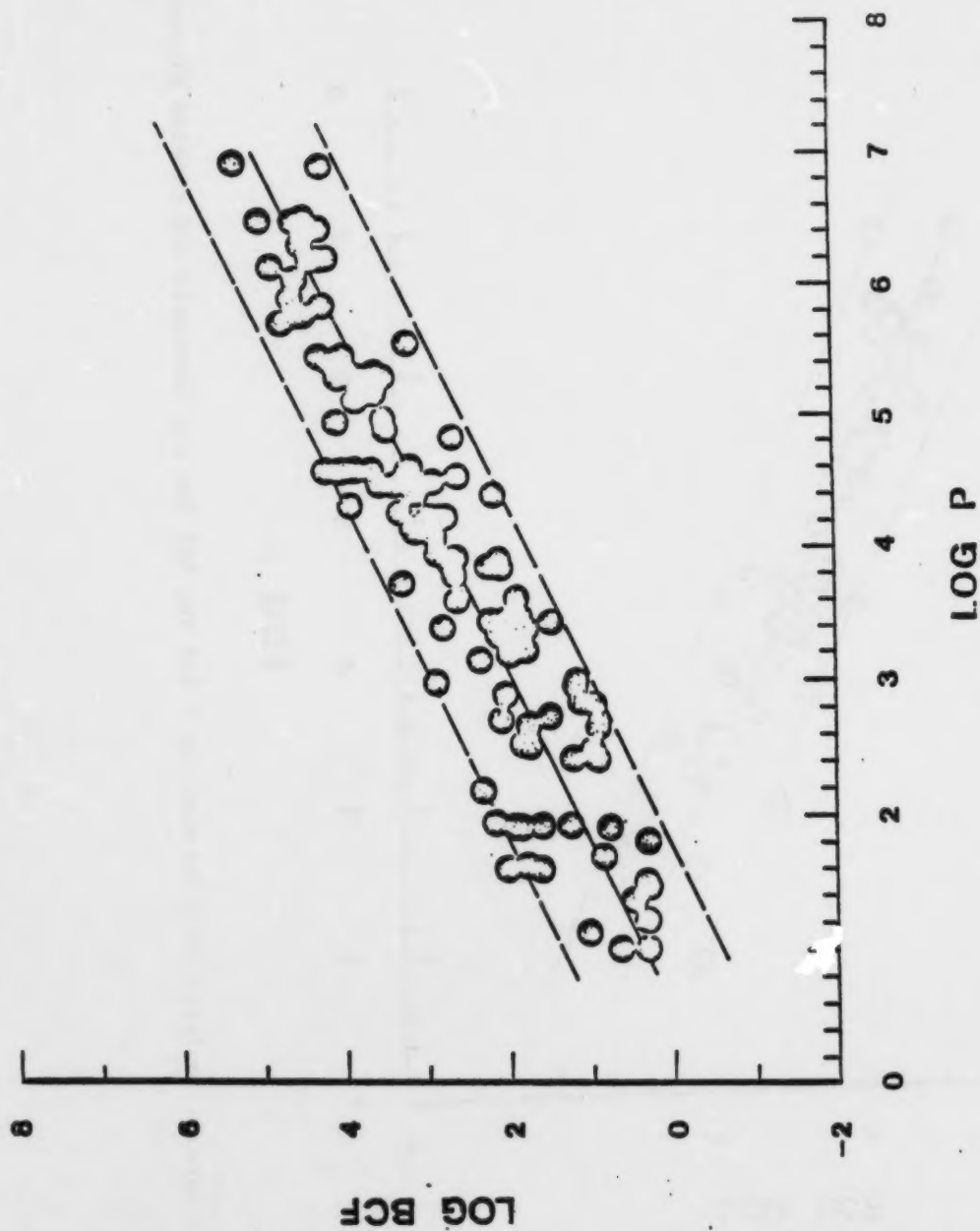


Figure 3. Relationship between $\log P$ and $\log BCF$ for all chemicals and all fish species.

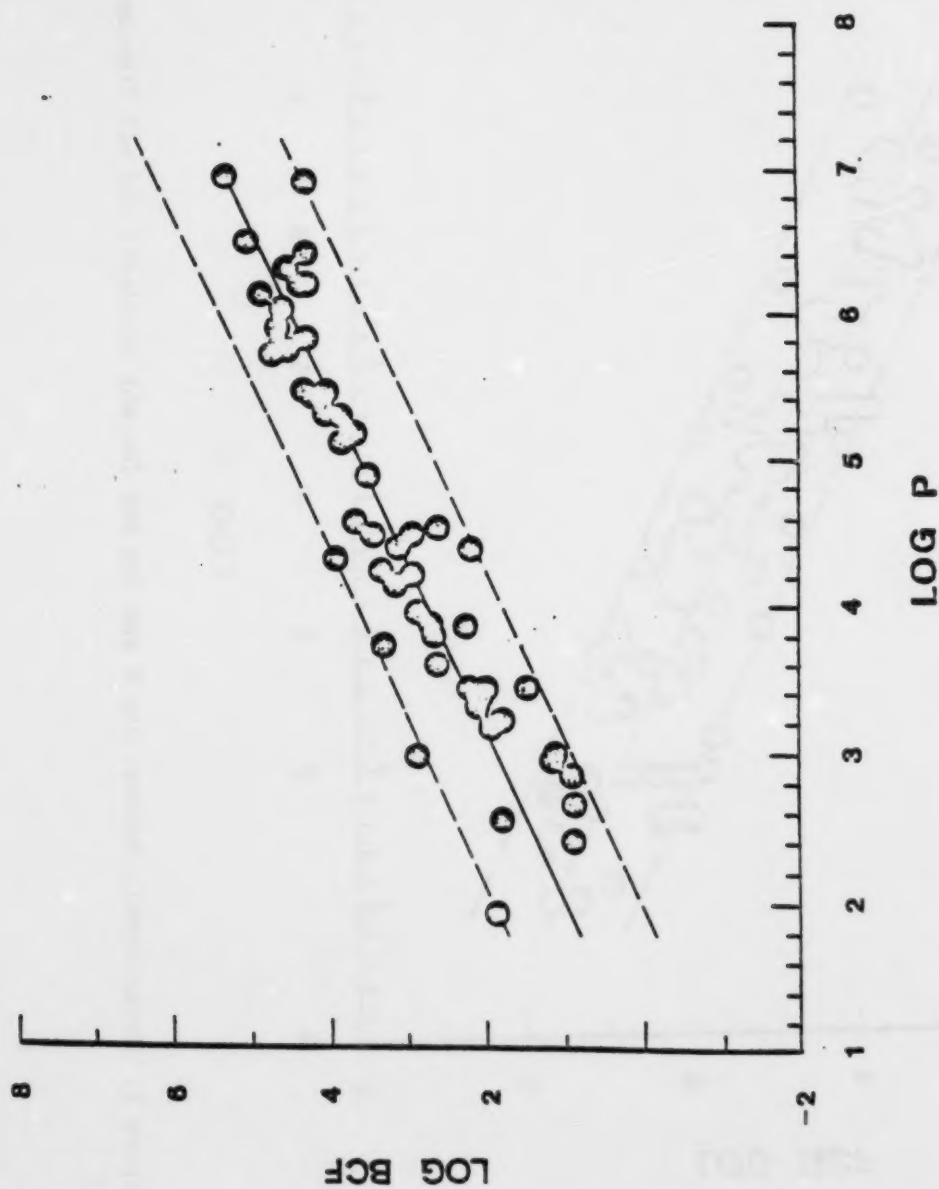


Figure 2. Relationship between $\log P$ and $\log BCF$ for all chemicals and fathead minnows.

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Estimating the Acute Toxicity of Narcotic Industrial
Chemicals to Fathead Minnows

by

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ABSTRACT

The overwhelming number of industrial chemicals either in commerce or in development precludes actual toxicity testing of each chemical and creates a need for initial screening techniques to focus efforts on those chemicals with the greatest potential for adverse environmental effects. One promising screening technique is the use of structure-activity relationship to estimate aquatic toxicity from chemical structure.

Selecting five major classes of industrial chemicals from the TSCA inventory, this paper presents a structure-activity relationship between the 96 hour LC50 with fathead minnows and the n-octanol/water partition coefficient which can be computed from structure. Common industrial alcohols, ketones, alkyl halides, ethers and benzenes are shown to cause lethality by the same mode of action of narcosis. Consequently, a single bilinear equation can adequately predict the 96 hour LC50 of all classes to fathead minnows.

Key Words - Aquatic toxicity, narcosis, structure-activity, relationships, industrial chemicals

INTRODUCTION

The inventory of industrial chemicals includes a large proportion of relatively innocuous chemicals. Cost-effective hazard assessment methods must use rapid screening techniques to estimate toxicity and to focus testing resources on the more toxic chemicals. Although few papers concerned with the lethality of industrial chemicals to aquatic organisms discuss the modes of action, we have observed that narcosis is a predominant mechanism of lethality among the less toxic chemicals.

Narcosis is a reversible state of arrested activity of various protoplasmic structures under the influence of chemicals and comprehensive reviews have been published (1-3). Ferguson (4) proposed that when such a physiological effect is reversible, an equilibrium exists between the organism and the external phase and the physiological effect is a function of external concentration, the toxic effect is physical in character. Physical toxicity will be exhibited by organic compounds at sufficient concentration unless it is masked by irreversible chemical effects related to specific functional groups within the molecule.

The physical nature of narcosis leads to effects which are chemically nonspecific as evidenced by the narcotic action of gases (5), aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, alcohols, ethers, ketones, aldehydes, weak acids and bases, and some aliphatic nitro-compounds (1,3,6).

Ferguson (4) and Mullins (7) proposed that the chemical thermodynamic activities of narcotics in blood at the point of equal effects are approximately equal, with some of the variability accounted for by variations in molecular volume. Because the chemical activity in blood is related to

the chemical concentration in blood through the activity coefficient which is difficult to measure, toxic responses are seldom based on chemical activity. The chemical activity of volatile narcotics in mammalian studies has been estimated from the partial pressure of the chemical causing narcosis through the expression:

$$A_{\text{nar}} = P_{\text{nar}}/P^{\circ}$$

where A_{nar} is the thermodynamic activity for narcosis, P_{nar} is the partial pressure for narcosis, and P° is the partial pressure for the pure narcotic.

For non-volatile chemicals in mammalian tests, A_{nar} is not easily determined. However, A_{nar} for non-volatile chemicals in aquatic tests can be estimated from the expression:

$$A_{\text{nar}} = \frac{C_{\text{nar}}}{C_s}$$

where C_{nar} is the narcotic concentration in water and C_s is the water solubility of the chemical. The estimation is expected to be valid provided the thermodynamic activity of the chemical in water is equal to the activity in the blood of the test organisms, i.e., the chemical in water is at equilibrium with that in blood. Under these conditions, the acute toxicity of narcotics to fish can be expected to be directly related to the water solubility of the chemical. This work presents an evaluation of this model in estimating aquatic toxicity of industrial narcotics.

EXPERIMENTAL PROCEDURES

Chemicals for this study were selected from the Toxic Substances Control Act industrial inventory. The 96-hr LC50 of the chemicals were determined for fathead minnows (Pimephales promelas) from the Environmental Research Laboratory-Duluth culture using flow-through proportional diluters (8) and test methods described by the U.S. Environmental Protection Agency Committee on Methods for Toxicity Tests with Aquatic Organisms (1975). Lake Superior water maintained at $25 \pm 1^\circ\text{C}$ was used in all tests. Routine measures of hardness and alkalinity of test water yielded mean values of 56.3 mg/l and 42.2 mg/l CaCO_3 , respectively. The arithmetic mean of the pH was 7.5 and dissolved oxygen was always greater than 60% of saturation.

Twenty-five 30-day old fish each weighing approximately 0.12 gm were randomly divided among 12 test tanks (control and five different concentrations each in duplicate). Fish were not fed during the test and deaths were recorded after 1, 3, 6, 12, 24, 48, 72, and 96 hours. Median lethal concentration, or LC50, was computed using the trimmed Spearman-Kärber method (9) on a PDP-11/70 computer.

Concentrations of chemicals in water were measured in each tank throughout the test. Water was analyzed either by UV-spectroscopy or by direct aqueous injection on a gas chromatograph (GC). GC analysis were performed on a Hewlett-Packard 5730A gas chromatograph equipped with flame ionization detectors and 122 cm x 2 mm i.d. columns filled with the porous polymer Tenax GC (Applied Science, Riviera Beach, FL). Column temperature was varied for each chemical between 100 and 225°C to provide optimum analytical conditions.

Water solubility of test chemical was obtained from the literature or determined experimentally. Chemicals were added to water in 500 ml flasks and gently shaken in a $25 \pm 1^\circ\text{C}$ water bath until the concentration was constant. Samples of saturated water were centrifuged for 30 minutes at 10,000 G, 25,000 G, and 40,000 G in separate centrifuge tubes. Water from each tube was removed for GC analysis. In general, the samples centrifuged at more than 10,000 G contained statistically identical concentrations as those centrifuged at 10,000 G and therefore all water solubility values were treated as replicates.

The values for n-octanol/water partition coefficients were taken from the monograph of Hansch and Leo (10). Those partition coefficients not previously measured were estimated by reverse phase liquid chromatography as described by Veith et al. (11) or calculated using the fragment constant method of Hansch and Leo (10).

0.04 of the water solubility if fish were similar in sensitivity and an equivalent equilibrium existed between the water and fish blood. Table 1 shows that the ratio of LC50/Cs varies from 0.015 for hexanol to 0.036 for nonanol. The activity (LC50/Cs) of higher homologs increases until the LC50 is greater than water solubility. The activity of miscible chemicals cannot be estimated from solubility; however, chemical activity at the LC50 can also be estimated by multiplying the LC50 by the activity coefficient of the chemicals. Although activity coefficient data in the literature are scarce, Amidon et al. (13) presented coefficients for six of these alcohols. The activities necessary for narcosis in fish computed from the activity coefficients are presented in the final column of Table 1. Not only do these estimates show excellent agreement with the estimates from water solubility, but also the mean activities of all lower homologs is approximately 0.025.

The increase in chemical activity observed for the higher homologs in this series may result from insufficient time to achieve a thermodynamic equilibrium between the water and lipid phases at water concentrations below 10^{-5} molar, or from a decrease in the chemical activity of bulkier chemicals occupying larger molecular volumes (7). Experiments to test these hypotheses are in progress in this laboratory.

The data in Table 1 is summarized by the bilinear equation:

$$\log \text{LC50} = -1.09 \log P + 1.09 \log (0.000068 P + 1) - 0.79$$

$$\text{where } R^2 = 0.9986.$$

To test whether this relationship accurately models the toxicity of other industrial chemicals which are acutely toxic via narcosis, the 96 hr LC50 of 45 other common chemicals from the industrial inventory were compiled in Table 2 and plotted on the alcohol model in Figure 2. These data indicate

general agreement between the narcosis equation using only $\log P$ as an independent variable and the observed LC50.

Although these data indicate that chemicals exerting a common mode of action may be modeled jointly, it is likely that more accurate estimations will require an individual structure-activity relationship for each class of chemicals as well as the use of electronic and steric factors in addition to $\log P$ as molecular descriptors. The literature suggests narcosis may not be a truly non-specific mode of action, but rather may consist of a series of different mechanisms such as membrane swelling and membrane depolarization which produce the same apparent effects. Data generated to date on ester and phenol toxicity indicate that the mode of action appears to be narcosis; however, these groups are slightly more toxic than other narcotics. Consequently, the correlation with $\log P$ presented in Figure 2 will likely become a "family" of lines for each class of chemical.

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Table I. Water Solubility, Partition Coefficient and Acute Toxicity of Common Alcohols to Fathead Minnows.

Chemical	96-hr LC50 mg/l	Log LC50 ^a	Cs (mg/l)	Log Cs ^a	Log P	LC50/Cs	Anar ^b
methanol	28,200	-0.06	+	+	-0.66	-	0.030
ethanol	14,700	-0.51	+	+	-0.16	-	0.027
2-propanol	10,400 (9,640) ^c	-0.80	+	+	0.14	-	0.025
1-butanol	1,740	-1.63	74,700	0.03	0.88	0.023	0.022
1-hexanol	97.2	-3.02	6,270	-1.21	2.03	0.015	
1-octanol	13.4	-4.00	587	-2.35	3.03	0.023	0.020
1-nonanol	5.7	-4.40	158	-3.00	3.53	0.036	
1-decanol	2.3	-4.84	34	-3.67	4.03	0.068	0.055
1-undecanol	1.04	-5.22	8.5	-4.31	4.53	0.122	
1-dodecanol	1.01	-5.27	1.9	-4.99	5.00	0.532	
1-tridecanol	*	*	0.33	-5.78	5.51	>1.0	

^a Expressed as moles/liter

^b Calculated from Anar = LC50(mg/l) x activity coefficient presented in Amidon et al. (1974)

^c Duplicate toxicity tests in parenthesis.

+ Miscible with water

* No fish mortality in saturated solution

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Table 2. Acute Toxicity of Other Industrial Chemicals to
Fathead Minnows.

Chemical	96-hr LC50 (mg/l)	Log LC50	Log P
<u>Alcohols</u>			
2-methyl-1-propanol	1,460	1.29	0.68
1-chloro-2-propanol	244	-2.58	0.85
2,2,2-trichloroethanol	298	-2.70	1.39
2,3-dibromopropanol	71	-3.49	1.52
cyclohexanol	705	-2.15	1.23
2-methyl-2,4-pentanediol	10,700	-1.03	-0.23
2-phenoxyethanol	346	-2.06	1.16
<u>Ketones</u>			
acetone	8,140 (7,310) ^c	-0.85	-0.24
2-butanone	3,200	-1.35	0.285
2-pentanone	1,530	-1.75	0.790
2-octanone	37	-3.54	2.77
5-nonanone	31	-3.57	2.79
2-decanone	5.7 (4.2) ^a	-4.44	4.24
7-tridecanone	*	*	5.53
3-methyl-2-butanone	868	-2.00	0.590
5-methyl-2-hexanone	158	-2.86	1.89
4-methyl-2-pentanone	509	-2.29	1.25
6-methyl-5-heptene-2-one	85.8	-3.17	2.18
3,3-dimethyl-2-butanone	86	-3.07	1.82
cyclohexanone	630 (732) ^d	-2.19	0.810
2-butanone oxime	844	-2.01	0.89

Table 2 (Continued)

Chemical	96-hr LC50 (mg/l)	Log LC50	Log P
acetophenone	161	-2.87	1.73
benzophenone	14.3 (15.2) ^a	-4.09	3.18
2,3,4-trichloroacetophenone	2.0	-5.00	3.66
2,4-dichloroacetophenone	11.7	-4.16	2.95
<u>Ethers</u>			
triethylene glycol	69,800	-0.33	-1.24
2-(2-ethoxy ethoxy) ethanol	26,400	-0.71	-0.08
t-butylmethyl ether	706	-2.10	1.06
diisopropyl ether	91.7	-3.05	1.74
di-n-butyl ether	32.5	-3.60	3.05
2,6-dimethoxytoluene	20.5	-3.88	2.87
diphenyl ether	4.0	-4.63	4.21
dipentyl ether	3.2	-4.70	4.17
p-nitrophenyl phenyl ether	2.7	-4.91	3.93
dioctyl ether	*	*	
<u>Alkyl Halides</u>			
1,2-dichloroethane	118	-2.92	1.76
1,1,2-trichloroethane	81.7	-3.21	2.28
1,1,2-trichloroethylene	44.1	-3.48	2.42
1,1,2,2-tetrachloroethane	20.3	-3.92	2.66
tetrachloroethylene	13.5	-4.08	2.95
pentachloroethane	7.3	-4.44	3.58
hexachloroethane	1.5	-5.19	4.23

Table 2 (Continued)

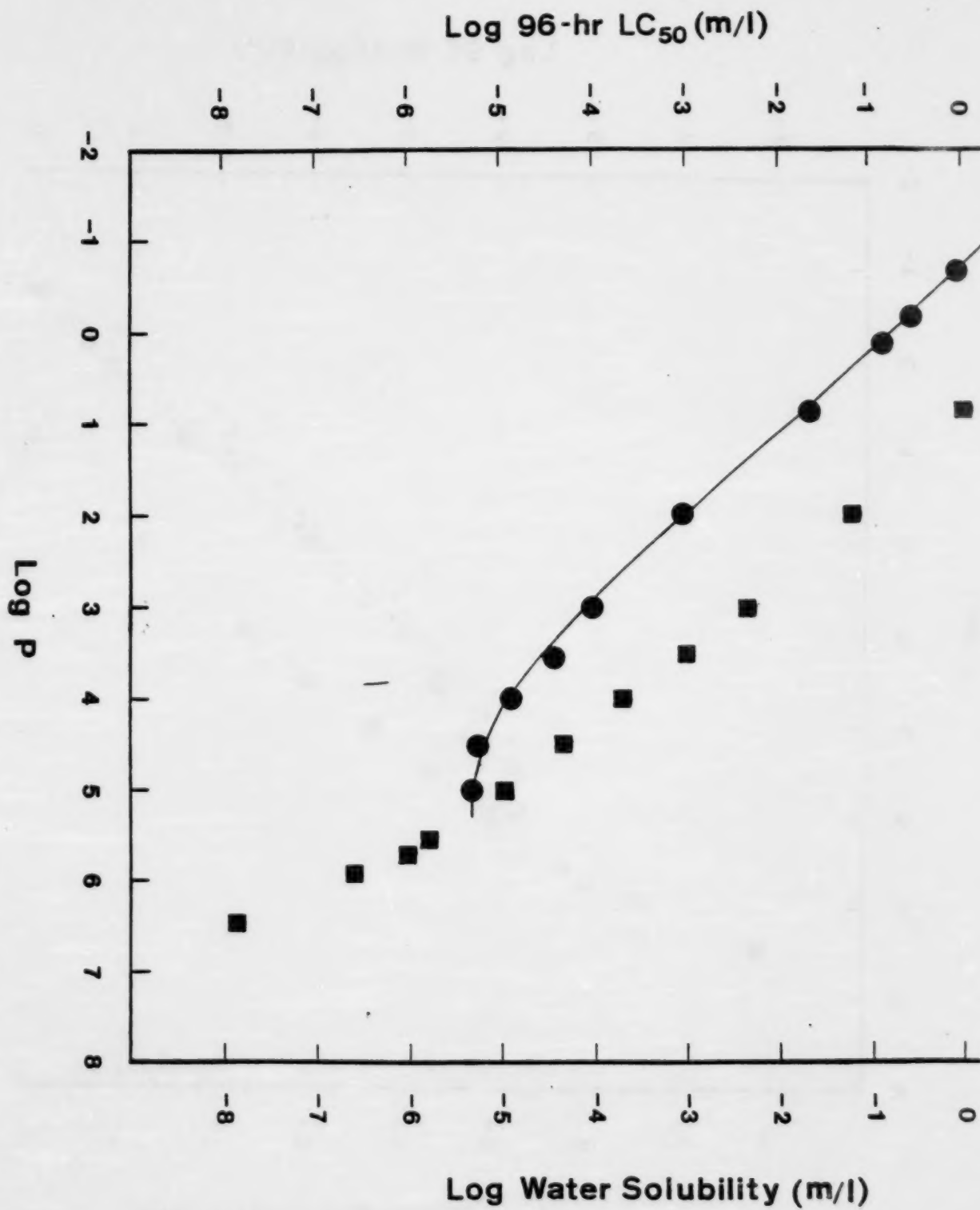
Chemical	96-hr LC50 (mg/l)	Log LC50	Log P
<u>Benzenes</u>			
1,3-dichlorobenzene	7.8	-4.28	3.38
1,4-dichlorobenzene	4.0	-4.56	3.35
1,2,4-trichlorobenzene	2.9	-4.80	4.20
1,2,3,4-tetrachlorobenzene	1.1	-5.30	4.94
pentachlorobenzene	*	*	5.69
hexachlorobenzene	*	*	6.44

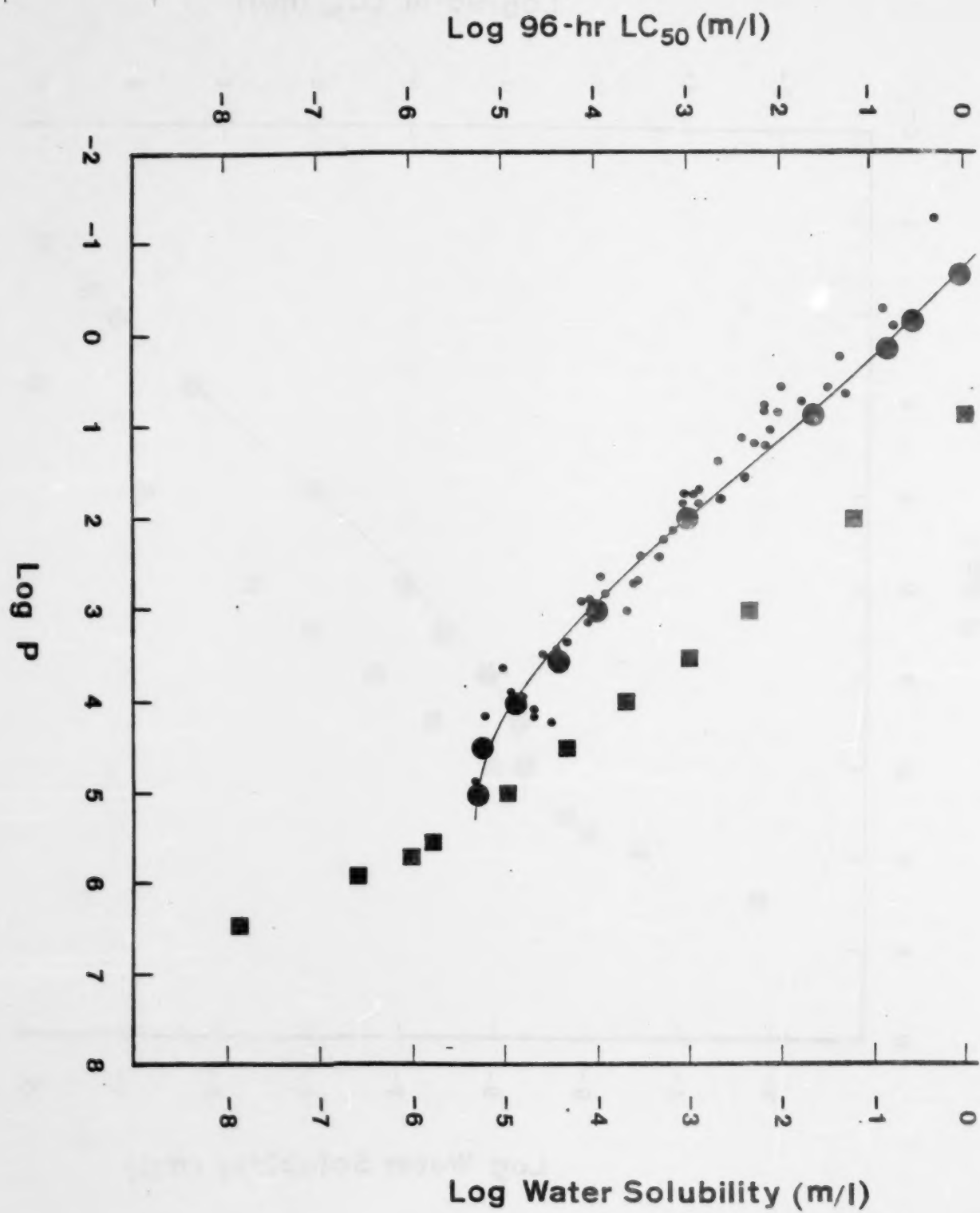
^a Duplicate toxicity tests in parenthesis.

* No fish mortality in saturated solution.

FIGURE CAPTIONS

1. Bilinear relationship between water solubility (squares) and 96-hr LC50 (circles) with log P for aliphatic alcohols.
2. Relationship between 96-hr LC50 (small circles) of narcotic chemicals and log P superimposed on bilinear alcohol model.





STATISTICAL STRUCTURE-ACTIVITY MODELS OF MAMMALIAN TOXICOLOGICAL ENDPOINTS

by

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The advent of the Toxic Substance Control Act stimulated us to apply the principles of structure-activity relations generally used in medicinal chemistry to the problem of estimating toxicological properties of chemicals based on their structure alone. Based on these estimates, one can then make preliminary decisions as to the relative importance of different chemicals. These decisions can be used as part of a comprehensive evaluation as to the action to be taken with specific compounds.

Models have been developed for rat oral LD₅₀, mutagenicity (Ames), carcinogenicity and teratogenicity. In this paper we briefly describe the results obtained with the rat oral LD₅₀, carcinogenicity and teratogenicity models.

The rat oral LD₅₀ model: This model is based (Figure 1) on 1,851 chemicals derived from the Registry of Toxic Effects of Chemical Substances (RTECS). Each chemical is described by a set of substructural parameters, molecular weight and sometimes octanol-water partition coefficient (Figure 2). A regression equation based on these parameters and modeling the inverse of the molar form of rat oral LD₅₀ ($\log 1/C$) was then developed. By means of this equation and the process shown in Figure 3, one can then calculate via a computer program the estimated rat oral LD₅₀ for untested chemicals. A typical computer output is shown in Figure 4. This output also includes diagnostic information used for quality control purposes to determine the level of quality of a calculated estimate.

A validation study based on approximately 600 chemicals which were not included in the data set from which the model was calculated, but for which the bioassay was performed shows that 50% of the chemicals are estimated by the equation within a factor of 2 of the measured value, and 85% within a factor of 4. These results make it evident that this structure-activity model for rat oral LD₅₀ can perform with the same level as quality as the animal bioassay.

The Carcinogenicity Model: This model is based on the Reviews of the International Agency for Research in Cancer in which compounds are classified as being definite carcinogens or indefinite carcinogens (Figure 5). The suspected carcinogen class was not used in the model. In this case a discriminant analysis model is constructed. This model produces an equation which maximally separates the positive from the negative compounds. Note that there are a total of 120 negatives and 223 positives. In the lower half of Figure 6 is a classification table which shows the performance of the discriminant model on the chemicals used in its development. Included are a certain number of compounds in what is called an indeterminate range, i.e. a range near probability of 0.5, i.e. chance. It is evident from this Table that approximately 4% of the chemicals are misclassified as false negatives and approximately 10% as false positives. A validation of this equation based on independent chemicals not included in the model shows that approximately 75% of the chemicals are classified by the equation as they are classified by animal experiments.

In Figure 7 we show the computer process necessary in order to generate these estimates of probability. In Figure 8 we show an example of the use of these estimates. The estimates are included among chemicals for which the endpoint has been obtained experimentally (marker compounds). In this fashion one can obtain an impression of where the chemicals for which estimates have been produced lie

with respect to those for which the endpoints have in fact been measured.

The Teratogenesis Model: The data for the teratogenesis model were obtained from a variety of sources shown in Figure 9. For each of the chemicals a score between 0 and 1 was assigned by a teratologist. Zero represents a chemical for which there is very adequate evidence of non-teratogenicity, 1 a compound which is a definite human teratogen. These scores and the chemicals to which they were assigned were then reviewed by three other teratologists and disagreements resolved. The chemicals with scores between 0 and .25 were then called non-teratogens and chemicals with scores .75 and above were called teratogens (Figure 10). A discriminant equation was again developed on the basis of these 430 chemicals (Figure 11) with the results shown in the classification matrix (Figure 12). One notes that the false positives amount to approximately 8% and the false negatives approximately 10%. An independent validation of this equation shows that 88% of the chemicals were correctly classified. In Figure 13 we show the computer process necessary to obtain these estimates, some of which are listed together with marker compounds in Figure 14.

Conclusion: Through the use of these statistical structure-activity models it is now possible to obtain estimates of a variety of toxicological endpoints for priority setting purposes. Work is currently planned or in progress to apply the same principles to rabbit eye and skin irritation, aquatic toxicity and biodegradability.



FIGURE 1

RAT ORAL LD₅₀ MODEL

Source of data:

RTECS (Registry of Toxic
Effects of Chemical Substances)

Number of chemicals: 1,851

Range of log 1/C: 1.25--4.75

FIGURE 2

DESCRIPTOR CANDIDATES

EACH COMPOUND IS DESCRIBED BY A SET OF PARAMETERS

OCTANOL-WATER PARTITION COEFFICIENT (OFTEN)

MOLECULAR WEIGHT

MOLAR REFRACTIVITY (OFTEN)

WLN-BASED SUBSTRUCTURAL KEYS

ORIGINAL CROSSBOW KEYS

NEW KEYS

SUSPECTED CARCINOGENIC STRUCTURES (FDA)

148

161

41

350

KEY TYPES

ALL PARTS OF MOLECULE

ALL NON-CYCLIC PARTS OF MOLECULE

CHAIN FRAGMENTS

SUBSTITUENT FRAGMENTS

RING HETEROATOMS

RING TYPES

RING FUSIONS

RING LINKAGES

TOTAL RING FEATURES

SUSPECTED CARCINOGENIC STRUCTURES

FIGURE 3

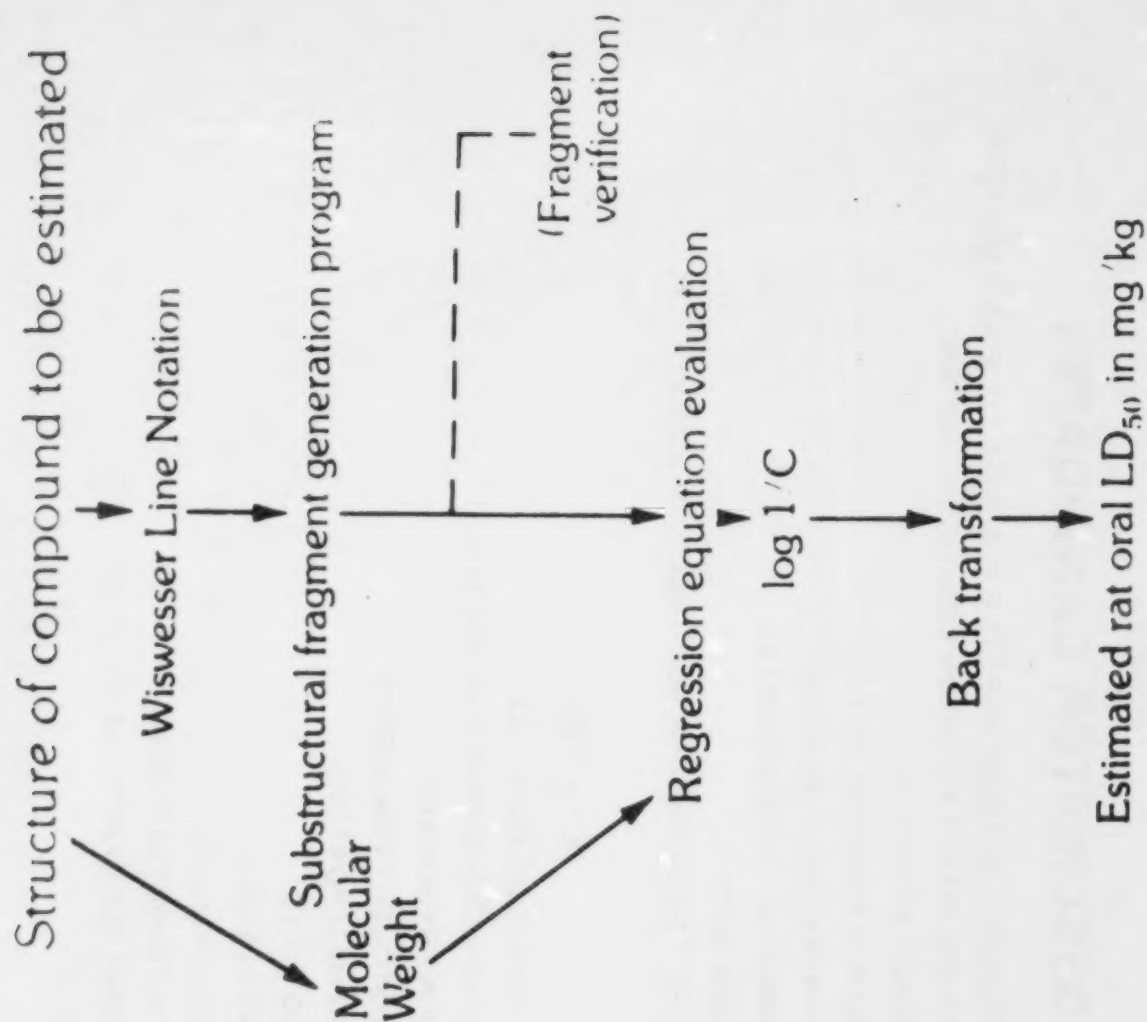


FIGURE 4

*** TOXICITY ESTIMATION SERVICE ***

REF NO. 50180
 MOLECULAR WEIGHT 125.60
 WLN T6MPOTJ B0 BN2C G

 -- ESTIMATION FROM THE RAT ORAL LD50 MODEL --

THE FOLLOWING 3 KEYS APPEAR IN BOTH THE ESTIMATING EQUATION
 AND THE COMPOUND. THEY WILL BE USED IN THE ESTIMATION.

5 312 315

THE FOLLOWING 13 KEYS APPEAR ONLY IN THE COMPOUND AND NOT IN
 THE ESTIMATING EQUATION. THEY WILL NOT BE USED IN THE ESTIMATION.

1 8 19 22 24 73 77 93 102 106 110 134
 143

--ALL KEYS IN THE COMPOUND WERE PRESENT IN THE DATA BASE
 THE RAT ORAL LD50 ESTIMATE IS 30.032 MG/KG

FIGURE 5

CARCINOGENESIS DATA

SOURCE: INTERNATIONAL AGENCY FOR RESEARCH IN
CANCER REVIEWS VOLS. 1-17

INDEFINITE		DEFINITE ANIMAL DEFINITE HUMAN	
ESTRIOL		ESTRADIOL	
RESORCINOL		BENZO[<i>a</i>]PYRENE	
CHOLESTEROI		ACTINOMYCIN D	
ANILINE		ESTRONE	
ISOPROPYL ALCOHOL		DIETHYLAMINE, <i>N</i> -NITRO-	
ETHYLENE OXIDE		2-OXETANONE	
BENZENE, <i>O</i> -DICHLORO-		ACETAMIDE	
ANTHRANILIC ACID		IODOMETHANE	
TOTALS	120		223
GRAND TOTAL			343

FIGURE 6

CLASSIFICATION MATRIX

THE INDETERMINATE REGION SPANS $P = 0.5$

DECISIONS ABOUT CARCINOGENICITY CANNOT BE MADE IN THIS REGION

CLASSIFICATION BY DISCRIMINANT EQUATION

	Non or Indefinite		Indeterminate		Definite	
	N	%	N	%	N	%
<u>INDETERMINATE: .4 - .599</u>						
NON OR INDEFINITE	96	80.0	10	8.33	14	11.7
DEFINITE	11	4.9	9	4.0	203	91.0
IARC CARCINOGEN CLASSIFICATION						
<u>INDETERMINATE: .3 - .699</u>						
NON OR INDEFINITE	93	77.5	14	11.7	13	10.8
DEFINITE	8	3.6	21	9.4	194	87.0
IARC CARCINOGEN CLASSIFICATION						

FIGURE 7

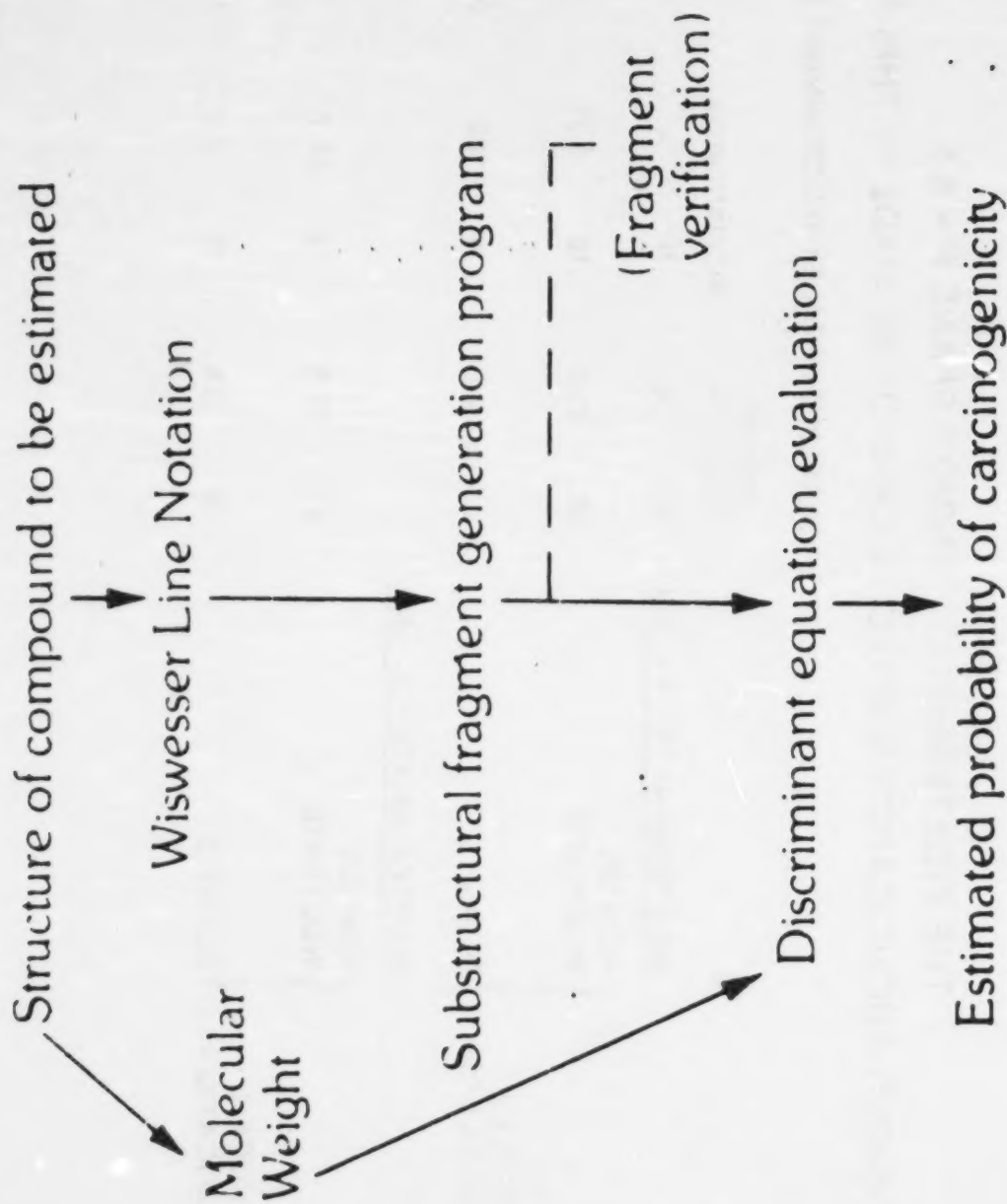


FIGURE 8

RANKED ESTIMATES CARCINOGENICITY

Rank	CAS #	Name	Recently Tested By NTP Dec. 80	Probability of Carcino- genesis	Marker
1	96-12-8	Dibromochloropropanol	(+) inhal mice/rats	.996	X
2	118-52-5	1,3-dichloro-5,5 dimethyl- hydantoin		.989	
3	91-59-8	2-naphthylamine		.983	X
4	116-14-3	Tetrafluoroethylene		.975	
5	75-38-7	Vinylidene fluoride		.838	
6	135-88-6	N-phenyl-2-naphthylamine		.567	X
7	108-46-3	Resorcinol		.072	X
8	56-75-7	Chloramphenicol		.013	
9	96-48-0	Dihydro-2 (3H) - furan		.003	X
10	2783-94-0	FSC Yellow No. 6	(-) oral mice/rats	0 0	X

FIGURE 9

TERATOGENESIS DATA

Sources: Schardein, J. Drugs as Teratogens
Shepard, Catalog of Teratogens, 3rd Edition
Environmental Teratogenesis Information Center

Criteria: For entry in Data Base: At least two mamalian species,
investigated by two reputable workers, after 1969.

Scoring: 0 to 1

EXAMPLES

Compound	Score
DDT	0.10
Phenylbutazone	0.05
Amitryptiline	0.10
Imipramine	0.10
Chlorambucil	0.90
Vinblastine	0.85
Mirex	0.80
Potassium Iodide	0.90
Diazepam	0.85
Vinyl Chloride	0.90

FIGURE 10

TERATOGENESIS SCORE DISTRIBUTION

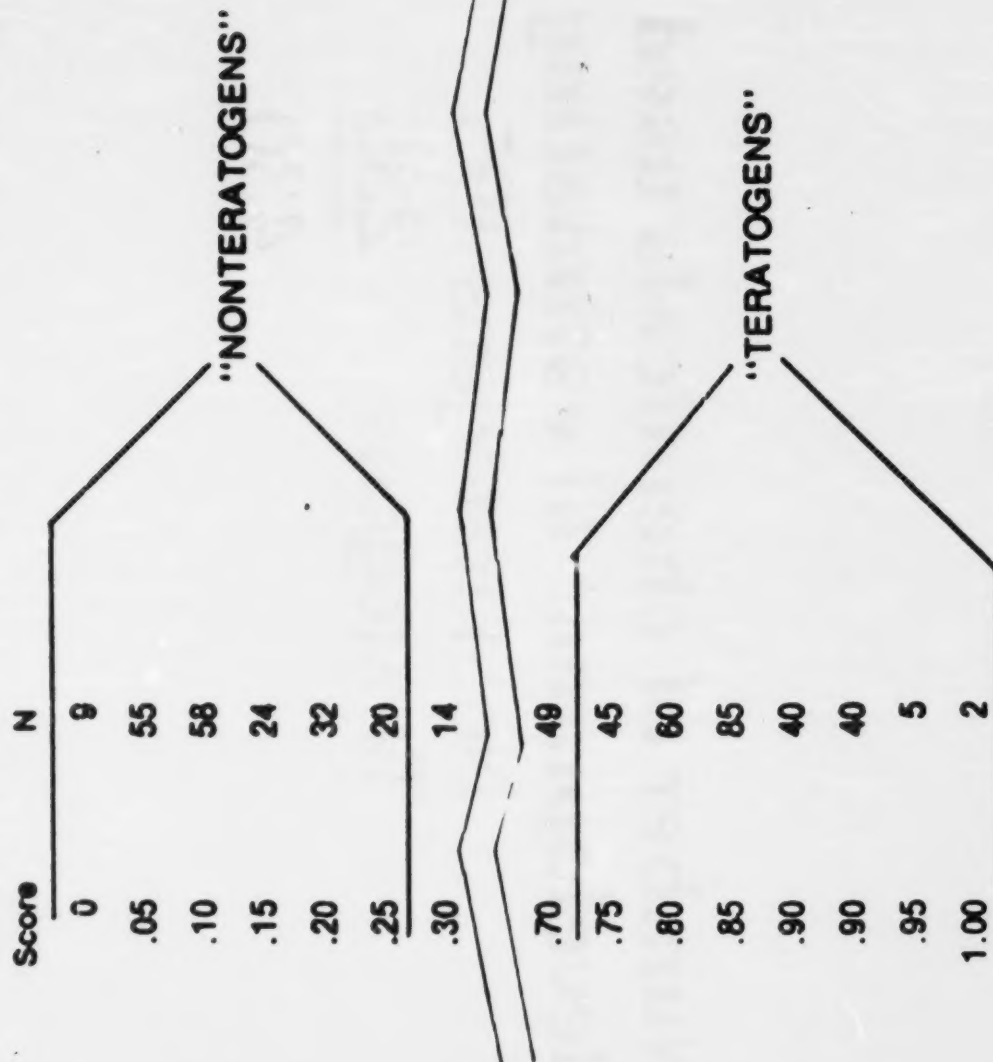


FIGURE 11

Number of chemicals used in development of estimating equation

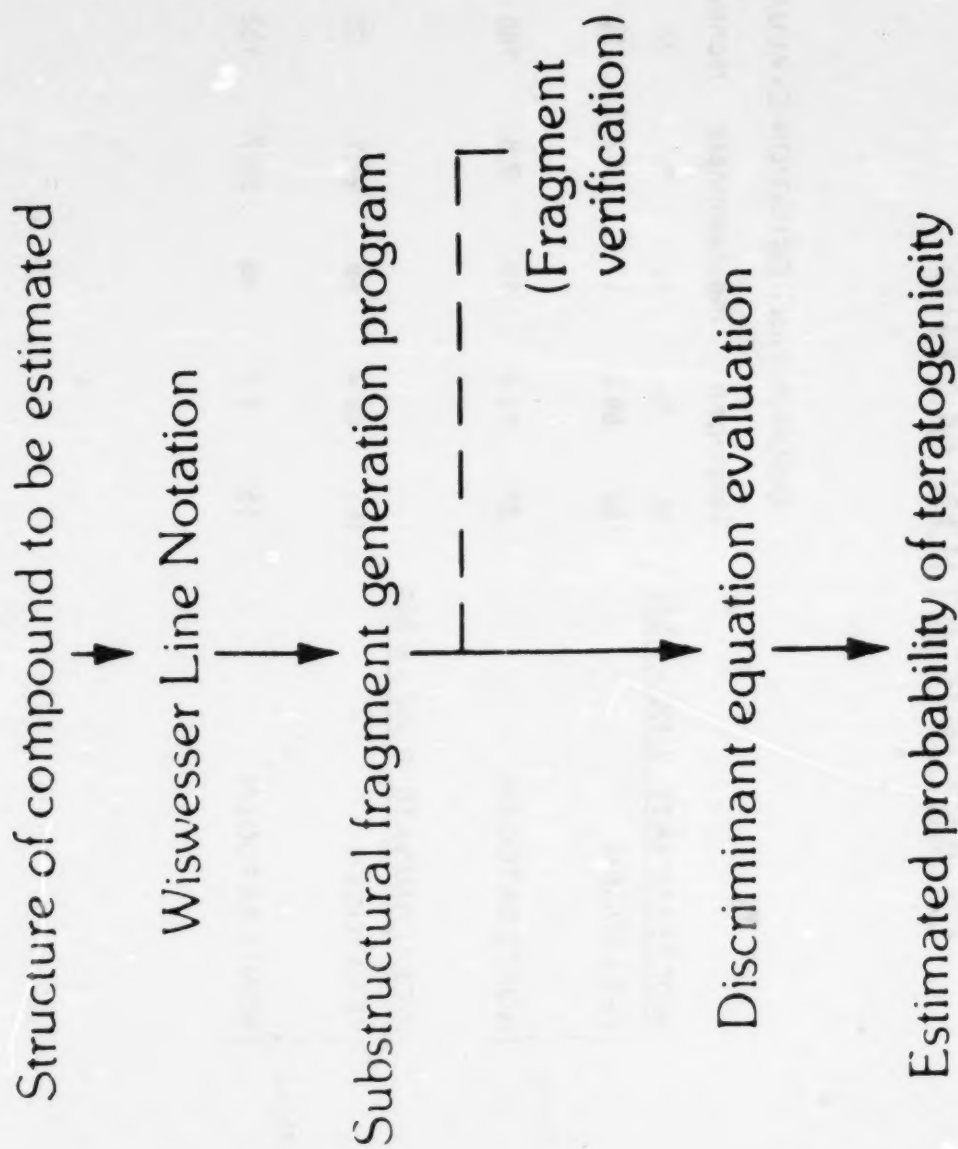
Nonteratogens	195
Teratogens	<u>235</u>
	430

FIGURE 12

CLASSIFICATION MATRIX

		DISCRIMINANT EQUATION EVALUATION					
		Teratogen		Indeterminate		Nonteratogen	
		N	%	N	%	N	%
ACTUAL CLASSIFICATION	<u>INDETERMINATE: 0.400 - 0.599</u>	186	80.2	17	7.3	29	12.5
	TERATOGEN						
	NONTERATOGEN	27	13.9	19	9.8	148	76.3
ACTUAL CLASSIFICATION	<u>INDETERMINATE: 0.300 - 0.699</u>	161	69.4	49	21.1	22	9.5
	TERATOGEN						
	NONTERATOGEN	15	7.7	46	23.7	133	68.6

FIGURE 13



UNTESTED COMPOUNDS TO BE EVALUATED FOR TERATOGENICITY

CAS #	COMPOUND	NTP SCHEDULED IN 1981
118-52-5	1,3-Dichloro-5,5-Dimethylidantoin	X
58-93-5	Hydrochlorothiazide	X
96-69-5	4,4-Thio bis(6- <i>t</i> -Butyl)- <i>m</i> -Cresol	X
110-82-7	Cyclohexane	X

MARKER COMPOUNDS — ENDPOINTS KNOWN

	Score
57-22-7 Vincristine	0.85
50-00-0 Formaldehyde	0.85
58-08-2 Caffeine	0.85
54-71-7 Pilocarpine HCl	0.40
56-81-5 Glycerine	0.00

ISHOW
An Information System for Hazardous Organics in Water

by

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All of us here today associated with the identification, evaluation, and control of toxic substances in industrial effluents have at many times experienced a need for information on chemicals in commerce and/or their manufacturers. For example, either we personally were interested in a chemical or set of chemicals or else we were directed to find information by a plant manager or project director. If information on only one chemical or one manufacturer is needed then the task, although formidable, is feasible. However, if information on a large number of compounds and/or manufacturers is needed then the time and effort required to gather the information can be excessive. Today I would like to share with you an information and storage system known as ISHOW--An Information System for Hazardous Organics in Water.

ISHOW is a computerized, interactive information storage and retrieval system for physical and chemical properties along with aquatic toxicity data on organic chemicals manufactured or imported in the Great Lakes watershed. The system, which is implemented on the University of Minnesota - Duluth Control Data Corporation Cyber 171 computer, searches and displays information on chemical compounds along with the manufacturers and importers of these compounds. The system is user oriented so that it is easy to search for information and print it out. Because there are numerous "HELP" messages in ISHOW, a user can type in "HELP" at almost any point in ISHOW and receive a message on how to proceed. A user manual is available though ISHOW could be used without one.

Of the 14600 compounds in ISHOW, the bulk of these are from the publicly available portion of the EPA Office of Toxic Substances Chemicals in Commerce Information System inventory. Because the emphasis of this project is on chemicals imported or manufactured in the Great Lakes states, only compounds imported or manufactured in the Great Lakes states of Minnesota, Wisconsin, Michigan, Illinois, Indiana and Ohio and the Great Lakes watershed area of Pennsylvania and New York were selected from the Chemicals in Commerce Information System inventory. In addition, about 2000 compounds were supplied by the International Joint Commission and approximately 1000 are of interest in structure-activity correlation studies.

ISHOW was developed in coordination with the Environmental Protection Agency's Region V Great Lakes Program Office and the International Joint Commission in order to (1) establish an interactive catalog of chemical, physical and aquatic toxicity data on chemicals in the Great Lakes

watershed, (2) provide a means to determine unavailable or unreliable data, (3) establish a data base for structure-activity correlation studies and hazard assessment, and (4) provide a system to relate data on chemicals to their manufacturers.

In ISHOW there are 19 properties of which 5 are totally searchable. The other 14 properties are available by way of predefined sets which I will mention later. The searchable properties consist of Chemical Abstracts Service Registry number, logarithm of the partition coefficient, molecular formula, molecular weight, and systematic, common, and trade names. These properties are listed here along with the number of compounds in ISHOW which have that property and also the abbreviation used in ISHOW when referring to these properties. Although 2358 of the compounds have at least one LOGP value associated with them, up to four LOGP values may be listed per compound. Many of the LOGP values are calculated ones. Each compound has at least one name associated with it although ISHOW contains about 46200 systematic, common and trade names --most of which came from the Chemicals in Commerce System inventory.

<u>SEARCHABLE PROPERTIES</u>		<u>CMPDS</u>
CAS	CAS REGISTRY NUMBER	14600
LOGP	LOG OF THE PARTITION COEFFICIENT	2358
MF	MOLECULAR FORMULA	14551
MW	MOLECULAR WEIGHT	7673
NAME	COMPOUND NAMES (total: 46200)	14600

Fourteen of the other properties are listed below with their abbreviations and the number of compounds which have at least one entry per compound. The bioconcentration factors can have up to four values per compound, the chronic toxicity up to five values, and acute aquatic toxicity up to ten values per compound. There is no limit to the number of manufacturers per compound.

<u>OTHER PROPERTIES</u>		<u>CMPDS</u>	<u>OTHER PROPERTIES (cont'd)</u>		<u>CMPDS</u>
BCF	BIOCONCENTRATION FACTOR	81	LC50	ACUTE AQUATIC TOXICITY	736
BOD	BIOCHEMICAL OXYGEN DEMAND	—	MFRS	MANUFACTURER INFORMATION	12772
BP	BOILING POINT	2732	PK	-LOG OF THE ACID DISSOCIATION CONSTANT	480
CTOX	CHRONIC AQUATIC TOXICITY	70	SOL	WATER SOLUBILITY	3133
FP	FREEZING POINT	3589	VP	VAPOR PRESSURE	1358
GC	GAS CHROMATOGRAPHIC RELATIVE RETENTION TIME	63	WLN	WISWESSER LINE NOTATION	3494
KOV	KOVATS INDEX	—	WQC	WATER QUALITY CRITERIA	47

The manufacturer information in ISHOW includes only the manufacturers or importers in states or portions of states in the Great Lakes watershed. The information consists of manufacturer name, address, EPA region, manufacturer identification number which corresponds to each plant site and a production code which indicates the poundage manufactured or imported for 1977.

In order to begin to use the ISHOW data base, you first must place a call to the University of Minnesota--Duluth Control Data Cyber 171 computer. Enter your user number, password, and select the batch subsystem. Entries made by the user are underlined. To get into the ISHOW program, type -ISHOW, and the ISHOW program will print out a heading and ask the user to enter a command.

```

81/07/29 13.09.22
U OF M, DULUTH - CDC CYBER 171 NOS 1.4-509/308
USER NUMBER: 0000000
PASSWORD:
XXXXXXXX
RECOVER/ SYSTEM: BATCH
SRFL,0.
-/ISHOW

"ISHOW" DATA BASE
INFORMATION SYSTEM FOR HAZARDOUS ORGANICS
IN WATER
VERSION 2.3
DATA SET 2.3: 14600

COMMAND?

```

The commands that can be used in ISHOW are given below. Of these the three that are most important are SEARCH, LIST and SHOW. The use of those three commands and some of the other commands will be explained.

ISHOW COMMANDS

Searching the Data Base: SEARCH	COMMAND? SEARCH
Search Refinement: MERGE INTERSECT	PROPERTY? CAS
Seeing the Results: PAGE PRINTER LIST VIEW	CAS NUMBER(S)? 514103,60355,107186,90714,107437
Showing Manufacturers and Other Information: SHOW	90714 IS NOT A LEGAL CAS NUMBER CAS 107437 IS NOT IN DATA BASE
Miscellaneous Commands: INFORM EXPLAIN DELETE END COMMAND STATUS HELP COMMENT "S" KEY	CAS NUMBER(S)? 9005792,111140 CAS NUMBER(S)? c/r SET 1 CONTAINS 5 COMPOUND(S) --DEFINED BY: S,CAS,514103,60355,107186,...

To find Chemical Abstracts Service registry numbers with ISHOW the user would begin by entering SEARCH followed by a carriage return as in the example above. ISHOW will prompt for the next piece of information; in this case, the property to be searched--the Chemical Abstracts Service registry

number. After entering your registry numbers without hyphens and separated by commas, ISHOW will inform you which numbers are not valid and which could not be found in the data base. ISHOW will then store the compounds found in a set. The sets are merely numbered consecutively as produced.

For a search on the log of the partition coefficient, either an exact value or a range of values may be entered. Below, a range of 4.00 to 5.00 is indicated by a colon between the endpoints of the range. A solvent may be specified by typing in the number of the desired solvent. If you don't know what solvents are available, type in HELP at this point and a short list will be printed out. In this case solvent number 1 which corresponds to octanol is typed in. The 165 compounds found are stored in set 2.

COMMAND? SEARCH

PROPERTY? MF

P (FOR PARTIAL) OR C (FOR COMPLETE)? C

MOLECULAR FORMULA? C6 H4.5 CL2

SET 3 CONTAINS 3 COMPOUNDS
—DEFINED BY: S,MF,C,C6 H4.5 CL2

COMMAND? SEARCH

PROPERTY? LOGP

LOGP VALUE OR RANGE? 4.00:5.00

SOLVENT(S)? 1

SET 2 CONTAINS 165 COMPOUNDS
—DEFINED BY: S,LOGP,4.00:5.00/1

In a molecular formula search there are two types of searches available--complete and partial. A "complete" search will find only the compounds which have the exact numbers and types of atoms you specify. A partial search will find compounds that contain the numbers and types of atoms you specify plus additional types of atoms. Above, a complete search is being done for 6 carbon atoms, 4-5 hydrogen atoms, and 2 chlorine atoms. The resulting set 3 would contain only compounds with those numbers and types of atoms.

Below is a "partial" MF search for 6 carbons, 3-8 hydrogens and 2-4 nitrogens. This search would find compounds with the types and numbers of atoms specified and other atom types such as oxygen or chlorine. 105 compounds were found and are stored in set 4.

COMMAND? SEARCH

PROPERTY? MF

P (FOR PARTIAL) OR C (FOR COMPLETE)? P

ENTER THE MOLECULAR FORMULA? C6 H3:8 N2:4

SET 4 CONTAINS 105 COMPOUNDS
—DEFINED BY: S,MF,P,C6 H3:8 N2:4

COMMAND? LIST

SET? 3

SET 3 CONTAINS 3 CMPDS W/ MF=C6 H4.5 CL2

PROPERTIES? NAME,MFR

MFR OPTIONS? MNAME,ADDRESS,MID,PROD,REG

NAME

MFR

BENZENE, 1,2-DI
CHLORO-

MID-0040014 PROD-3 M-- REG-05
DOVER CHEMICAL CORP
15TH AND DAVIS ST
DOVER OH 44622

:

:

Now that a few sets have been formed we might want to look at the results. To do this the LIST command is used as above. ISHOW prompts the user to enter the number of the set he wants listed, gives a reminder of the contents of that set, and asks for the properties to be listed. At this point the user enters the abbreviations for the properties. In this case only name and manufacturer are entered because of space limitations. More properties could be entered and in fact all properties can be obtained for each compound. Because there are a number of items that may be listed for each manufacturer, ISHOW will prompt for them. Here all of them are entered - manufacturer name, address, manufacturer ID, production code and EPA region. A portion of the results are printed out.

This last example for a searchable property given below is for compound name. When ISHOW prompts for a name, enter it exactly. If it is in the data base ISHOW will print out its registry number. If it is not in the data base, you will get a message stating that no compound has been found. ISHOW will continue to ask for another name to be entered until only a carriage return is given. In this example ISHOW found 3 compounds that had a name of DPA and placed those compounds in set 5.

COMMAND? SEARCH

PROPERTY? NAME

NAME? DPA

CAS REG= 75990 DPA
CAS REG= 122394 DPA
CAS REG= 709988 DPA

NAME? /

SET 5 CONTAINS 3 COMPOUNDS
—DEFINED BY: S,NAME,DPA

COMMAND? INFORM

U (FOR USER DEFINED) OR P (FOR PREDEFINED)? U

SET	DETAIL	CPDS
3	S,NAME,DPA	3
4	S,MF,P,C6 H3:8 N2:4	67
3	S,MF,C,C6 H4:5 CL2	3
2	S,LOGP,4.00-5.00/1	134
1	S,CAS,514103,60355,107186,...	5

Because it is sometimes hard to remember what compounds are stored on which set, ISHOW has an INFORM command which will give you this information in table form. Included is a short description of how the set was formed and the number of compounds in the set. Listed above are the sets formed so far. The "S" in the detail column stands for search.

In addition to the sets formed by searches, ISHOW has a number of predefined sets available as soon as you get into the program. These sets include the compounds that have data for a particular property and are simply named by the abbreviation for the property name. For example, set BCF would contain all compounds which have at least 1 bioconcentration factor associated with them. There are predefined sets for the properties listed below. The last set on the list, set DB, which stands for data base, is the set of all compounds in the ISHOW data base.

PREDEFINED SETS

BCF	GC	SOL
BOD	KOV	VP
BP	LC50	WLN
CTOX	MP	WQC
FP	PK	DB

COMMAND? INTERSECTSETS? 2,LC50SET 6 CONTAINS 35 COMPOUNDS
--DEFINED BY: 1,2,LC50

Either the sets created by the user or the predefined sets may be merged or intersected as in set theory. Above is an example of intersecting a user defined set with a predefined set. Set 2 which contains 165 compounds with LOGP values between 4 and 5 in octanol is intersected with the predefined set of all compounds that have LC50 values. The results are stored in set 6.

To see the results of set 6 the LIST command is used as below and set 6 is specified. ISHOW asks for the properties you would like to see, and only NAME and LC50 are specified because of space limitations on the slide. The user is then reminded of the contents of set 6.

COMMAND? LISTSET? 6PROPERTIES? NAME,LC50SET 6 CONTAINS 35 COMPOUNDS
--DEFINED BY: 1,2,LC50

NAME	LC50	SPEC	TIM	TC	FN	REF
COUMAPHOS	+1.8+2	2	96			93d
	+4.6+2	14	48			900

(prints out 20 lines of results)

PAGE? 0DO YOU WANT RESULTS ADDED TO THE "PRINTER"
FILE? YES

ISHOW will begin to print out the LC50 values for coumaphos. The LC50 values are listed in a shorthand method. +1.8+2 would be read as 1.8 x 10 to the 2nd power in parts per billion. Other information listed with the LC50 value are a species number corresponding to the species on which the test was run, the time of the test in hours, test conditions indicating static, flow-through, or renewal bioassay, if known, a footnote number which would refer to additional comments and a reference number. After ISHOW has printed out 20 lines, which by default is defined as 1 page, ISHOW will ask if you would like to see another page of 20 lines. If so, give a carriage return at this point. This feature is handy if you are on a CRT terminal and want to look at the results before they pass by on the screen. If you are on a hard copy terminal, you might want to see more than 20 lines at a time. To the PAGE? prompt, type in the number of lines you would like to see and ISHOW will redefine the page length to that number of lines. If you do not want to see any more lines of results, type in a zero. If the printer feature has been turned on previously, ISHOW will inquire if you want the results stored on a temporary file named printer. At the end of your session this file may be sent to the line printer.

Besides the PAGE and PRINTER features which enhance the LIST command, another command that affects the LISTing of results is the VIEW command. The main advantage of the VIEW command is that the user can limit the output of the LIST command to only those compounds produced or imported in a specific geographic area. This applies to any sets of compounds created previous to turning on the VIEW command or any sets of compounds produced after that point. The VIEW window can be defined in three ways--by EPA region, states, or zipcodes.

Below is an example of the VIEW window being defined for the state of IL. In return you get a message with the total number of compounds produced or imported in the state of IL. If you want to see what temporary changes have occurred in the sets you created previously, use the INFORM command. Now the inform feature includes your current VIEW window and tells you how many compounds in each set are manufactured or imported in the state of IL. Now if the LIST command is used, the only compounds listed will be the ones in the viewing area of IL.

COMMAND? VIEW
WINDOW? STATE
STATE? IL
BUILDING THE VIEW WINDOW ...

3272 COMPOUNDS (MAXIMUM) WITHIN STATE, IL

COMMAND? INFORM, U

CURRENT VIEW WINDOW: STATE, IL

SET	DETAIL	CPDS	IN VIEW
6	I,2,LC50	35	4
5	S,NAME,DPA	3	0
4	S,MP,P,C6 H3:8 N2:4	105	9
:	:	:	:

COMMAND? SEARCH

PROPERTY? MW

MW OR RANGE? 150:170

SET 7 CONTAINS 797 COMPOUNDS
--DEFINED BY: S,MW,150.00:170.00
-- 60 COMPOUND(S) WITHIN STATE, IL

Above is a MW search when the VIEW window is defined as IL. Note that ISHOW will inform you of the number of compounds in the resulting set without the VIEW area specified and will also state the number of compounds included in the VIEW area. If the contents of set 7 are listed, 67 compounds would be printed out. When the VIEW feature is turned off, all commands and sets return to normal and a listing of set 7 would contain all 797 compounds.

One of the three most important commands in ISHOW is the SHOW command. By using this command the user can obtain the systematic, common, and trade names that ISHOW contains. You can find the species, solvents, references, and footnotes that are associated with the numbers assigned them. And finally, you can obtain manufacturer information by specifying state(s), city, zipcode(s), manufacturer name, manufacturer identification number, or EPA region.

Once the SHOW command is entered, ISHOW will prompt for one of the six items that can be entered. In the case below, names of compounds are being

sought. They can be identified by a set number or CAS registry numbers. Set number 5, which contained 3 compounds named DPA, was entered, and a portion of the results are shown.

```
COMMAND? SHOW
ITEM? NAMES
SPECIFIED BY? SET
SET? 5

SET 5 CONTAINS 3 COMPOUNDS
--DEFINED BY: 5, NAME, DPA
```

```
-- CAS = 75990
ALATEX
BASINEX P
DALAPON
DAWPN-RAE
DOWPN M
DPA
:
```

```
COMMAND? SHOW
ITEM? MFRS
MFRS LOCATED BY? ZIP
ZIP(S)? 60003,60005-60020,60025
COMPOUND PROPERTIES? c/s
```

```
DELAMAR, INC.
MID=007595J 2653 GREENLEAF
REGION=5 ELK GROVE VILLAGE, IL 60007
```

```
DENA CORP.
MID=007581D 850 NICHOLAS BLVD.
REGION=5 ELK GROVE VILLAGE, IL 60007
:
:
```

Above is an example of showing manufacturers by zipcode. The zipcodes are entered separated by commas and once again a range is indicated by a colon between the endpoints. You may also see the compounds manufactured or imported by each manufacturer. In this case that option was declined. ISHOW will inform you of the number of manufacturers found and begin printing them out. The PAGE and PRINTER features mentioned with the LIST command also work for the output of the SHOW command.

Below is an example of showing manufacturer information by manufacturer name. Enough of the manufacturer name must be entered to insure uniqueness. Note that the commands and other information that the user enters may be typed on one line separated by commas. This feature can save time for a more experienced user of ISHOW.

```
COMMAND? SHOW,MFRS,MNAME,DOW CHEMICAL
COMPOUND PROPERTIES? c/s
```

```
DOW CHEMICAL U.S.A. HANGING ROCK PLANT
MID=0013431 ROUTE 2 BOX 253
REGION=5 BRONTON OH 45638
```

```
DOW CHEMICAL CO. U.S.A. MICHIGAN DIVISION
MID=001024G 809 E. MAIN STREET
REGION=5 MIDLAND MI 48640
:
:
```

```
COMMAND? SHOW,MFRS,STATE,PA
COMPOUND PROPERTIES? CAS,NAME
```

```
HUGHSON CHEMICALS COOK ROAD
MID=006088Z P.O. BOX 556
REGION=3 SAEGERTOWN PA 16433
```

CAS	NAME
9020842	SODIUM POLYPROPOXYOCTYL SULFATE
9040806	TOLUENE DIISOCYANATE, TRIMETHYLOL
	PROPANE, PROPYLENE GLYCOL POLYMER
:	:

In the case above of showing manufacturers for Pennsylvania, we ask to see the compounds manufactured or imported also. Properties can be specified. Only Chemical Abstracts registry number and name are specified because of space limitations but any of the properties could be entered.

ISHOW would then print out the results.

It may appear that the same information can be obtained by showing manufacturers with property information as can be found by doing a search for compounds. This is somewhat true. The main difference is- that the SEARCH command always finds information via compounds while the SHOW manufacturers command obtains information via manufacturers.

I hope this gives you a good idea of the contents of ISHOW and how to use it. If any of you are interested in accessing ISHOW, you may write to me at the University of Minnesota, Duluth.

EPA WORKSHOP
CHICAGO, ILLINOIS

June 16, 1982

ESTIMATING IMPORTANT MOLECULAR PROPERTIES OF BIOLOGICALLY ACTIVE MOLECULES

Max M. Marsh

The challenge to understand drug action at the molecular level has attracted outstanding research scientists from all the major disciplines. With the exhilarating prospect that understanding can lead to prediction, "drug design" has become a "buzz-phrase" of the 80's. Every major pharmaceutical firm and most university medicinal chemistry groups in the world have such a formal or informal organization. Usually, this is a loose interdisciplinary federation comprising members with backgrounds in chemistry (including biochemistry, drug metabolism, and pharmaceutical chemistry), physics, mathematics, and pharmacology. The result is a mixture of approaches to a therapeutic problem, ranging from experimental to theoretical. Aside from the intellectual satisfaction to be derived from explaining how a certain compound exerts its biological effect, several practical considerations have contributed to the growing popularity of the molecular design effort; among these is the fact that even today, about 8000 compounds are synthesized and given preliminary biological activity tests for every one that becomes a useful drug. Another element is the fact that there is no shortage of leads among biologically active agents; consequently, there is almost always some compound already known with the baseline biological activity for a given therapeutic or toxicologic problem. This fact has significance to be pointed out later in regard to the value of estimated comparative properties of molecules. A corollary to this observation of the existence of a plethora of

leads is a possible necessity for a reorientation of thought about molecular design to focus on the elimination of undesirable side effects, often due to insufficient selectivity in terms of interaction with a target or "receptor".

For several years, the research group with which I have been associated has been concerned with molecular design from a point of view more theoretical than experimental, but with a realization that results arrived at on a theoretical basis must confirm experiment in order for the theoretical procedure to have predictive value. From these comments, it is apparent that our estimations of important molecular properties generally involve computational methods. First of all, however, we wish to decide which molecular properties in a design study are, in fact, important. For this purpose, a logical biochemical model of drug action is needed - and a significant feature of our group's approach has been the development of such models. Of course, there are instances where a reasonable model doesn't exist and we've resorted to empirical structure-activity correlation attempts; but that is not a preferred method. The relative merits of empirical statistical correlation methods compared to the biochemical model rationale are not critical to today's discussion, however. Instead, the focus is on the philosophy of selection of various molecular properties to be examined for their relationship to biological activity.

I think it is evident that there can be several levels of understanding with regard to the interaction of a biologically active compound and its receptor. One may "understand" the drug effect in terms of a whole animal or plant response, an effect on a single organ or tissue, the modulation of some kinetic or static cellular function, binding of the active substance to a target organelle (mitochondria, membrane), binding to a specific macromolecule or aggregate, or in terms of intermolecular forces between binding molecules

along with their stereodynamic distributions. Each of these levels entertains its own more or less baffling set of complexities; however, the last one offers some hope of resolution in terms of molecular design parameters - e.g., on a mathematical basis. Another way of looking at this is the replacement of biological or chemical intuition with "physical intuition".

We view the interaction of two molecules (more generally, molecular surfaces) as having up to five known force components: electrostatic (coulombic), hydrogen bonding, donor-acceptor (charge transfer), dispersion (London, VDW), and hydrophobic. As the molecules approach each other along a path called the reaction coordinate, these forces come into play with varying intensities. Eventually, some equilibrium position of the complex is reached; this may either be a non-covalently bonded state, or one or more covalent bonds are formed, resulting in a new molecular species. The development of a covalent attachment between a drug and its receptor generally requires the momentary existence of one or more intermediate structures or transition states. The tools of the theoretical chemist are most useful in the study of such intermediates which are seldom identifiable experimentally - and then only in rather indirect fashion - e.g., electronic or vibrational spectroscopy or ESR. Computational "snapshot" models of transition states are becoming more important in molecular design efforts, and several enzyme inhibitors of this type have been made. These compounds, modelled after a substrate transition state or intermediate structure, are often more potent inhibitors than the corresponding ground state analogs; two effects can contribute to such improvement - (1) an altered conformation of a part of the molecule can offer new or, additional binding sites, (2) energy required to distort the ground state geometry of an inhibitor in the direction of the transition state is not utilized, thereby increasing the stabilization energy of the enzyme-inhibitor complex.

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Non-covalently bound complexes of drugs and their receptors offer intriguing analytical problems, as well. Here the interactions are generally not as energetic as in the case of covalent binding, but molecular geometry and the various manifestations of electronic effects are equally important.

Ideally, knowledge of a drug receptor surface in atomic dimensions will permit the design of a complementary molecular structure, employing one or more of the interaction forces described previously; the prediction of a sterically appropriate assembly of functional groups on a synthetically and conformationally feasible skeleton is then a rather involved but entirely reasonable task. The crystal structures of many proteins - e.g., enzymes - of interest as drug targets have been reported; recently, a few oligonucleotides have had their structures elucidated, as well. These molecules are drug receptors, resolved at atomic dimensions, in the eyes of the physical scientist although the pharmacologist may consider that an incomplete definition. However, in practice, the molecular surface characteristics of the drug target often are not known and one must examine the common characteristics of a series of agonists and/or antagonists for clues to a meaningful biochemical model.

The methods for computing such properties as electronic charge distributions, bond strengths, ease of removal or acceptance of an electron, molecular electrostatic potential maps, or other electronic or energetic property are principally the semi-empirical ones in which the calculations are somewhat simplified through the use of parameters. The parameters are adjusted so that the calculated results fit observed properties of a representative series of molecules; the parameterized treatment is then presumed to be applicable to non-observable properties and to hypothetical molecules. The absolute values of such computed properties are often not very

realistic because of the simplifications required to make the computations tractable on drug-size molecules; however, most molecular design problems can be posed in comparative terms, so that relative values of calculated properties may be usefully ranked among compounds in a structurally related series. With increasing internal computer speeds and the growing utilization of parallel processing hardware, non-parameterized or ab initio calculations on molecules of biological interest are becoming feasible. These improvements will lead to better absolute values of calculated properties and concomitant opportunities to compare compounds which are only distantly related chemically, but have similar biological activities.

Other molecular properties, such as preferred conformations or hydrophobic interactions may be dealt with by non-quantum chemical methods. These may have classical physical concepts as a basis for the calculational method - e.g., classical mechanics for conformational energy calculations - or may be thermodynamically based, as in the view of hydrophobic interaction as an entropy-driven process. Molecular size is not a serious limitation in these calculations; however, they are empirical in nature and make use of several logical assumptions.

I would like to call to your attention the fact that all the preceding discussion may be viewed from the perspective of a growing new sub-discipline in the scientific community - that of "computational chemistry". Acknowledgement of its importance is evident in the creation of a Computers in Chemistry Division of the American Chemical Society a few years ago and, more recently, the publication on a continuing basis of the Journal of Computational Chemistry. The flourishing activities of the Quantum Chemistry Program Exchange located at the Chemistry Department of Indiana University offer first-hand knowledge of the rapidly expanding applications of the computational chemical approach.

What I have tried to do in a brief and not very profound way is to sketch a philosophy of the design of molecules with biologically interesting properties based on a view somewhat nearer first principles than screening and analogy. As a conclusion to this discussion, I offer some guiding principles for the utilization of calculational methods:

1. All methods currently applicable to medium-size (12-50 atoms) molecules have some constraints on their use.
2. The spectrum of utility varies among the different methods. Fortunately, the forces in molecule-receptor interactions are treatable - selectively - by these methods. Some treatments are more complete than others - e.g. electrostatic vs. hydrophobic interactions. The appropriate level of sophistication is not always evident and must be evaluated.
3. In general, solvent effects have not been included in the evaluation of ligand-receptor interactions; experience indicates that omission of this modulation of forces is often acceptable. The reason probably lies in the fact that many such reactions occur in a non-aqueous environment; it may also be reasonable to expect that solvation effects in a related series are nearly constant.
4. Where feasible, more than one calculational method is employed in a study, and more than one set of property relationships is examined - e.g. lone pair orbital populations, relative bond orders, and relative energies will all be compared in evaluating a hydrogen bond model.
5. Quantitation is at best approximate and is only useful in approximate terms - regardless of the number of digits. Any comparison with biological activity data is automatically limited by the precision of that data. Useful correlations based on more than one or two independent variables are seldom found.

COST EFFECTIVE APPROACHES
TO
EVALUATING AQUATIC SAFETY OF CHEMICALS

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IDENTIFICATION, EVALUATION, AND CONTROL OF
TOXIC SUBSTANCES IN INDUSTRIAL EFFULENTS

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ABSTRACT

The need to use cost effective methods to assess the environmental safety of a large number of chemicals and effluents has been the driving force to develop and evaluate new tools for safety assessment. Traditional aquatic safety assessments have relied upon data collected in a sequence of tiers to calculate a margin of safety between the estimated environmental exposure concentrations and measured toxicological effects. The exposure and effects data are refined in latter tiers such that the confidence in the margin of safety is increased. We employ a new approach using physical/chemical properties of organic chemicals to obtain information on the partitioning of chemicals to key compartments in the environment and earlier cost effective estimates of environmental exposure concentrations with a minimum of data.

In the area of effluents, no systematic approach has been widely accepted for safety assessment. The adoption of an assessment method based on the use of safety factors is long overdue. We propose the use of a tier approach consistent with the safety assessment techniques currently used to assess individual chemicals. This approach considers a series of acute and chronic aquatic tests and field testing, if necessary, to determine the toxicity of the effluent. The exposure concentration is based upon the percentage effluent present in the receiving water after complete mixing. This approach maximizes the use of available dilution for the effluent and provides for early estimates of safety factors with a minimum of data.

INTRODUCTION

In today's environmentally conscious world, there is a need to test chemicals and effluents for safety to man and the environment. The critical question is: How much testing is needed to better satisfy the regulators, citizens, environmentalists and producers that chemicals and effluents are not harmful when used and disposed of properly? We can do much to attain our goal of protecting the environment if we utilize the state-of-the-art techniques which will focus most of our attention on chemicals and effluents that have the greatest potential to adversely impact our environment.

For the protection of aquatic ecosystems, the principles are generally accepted on the use of tier testing and decision making based upon the relationship between environmental exposure and biological effects concentrations; i.e., a safety margin (1). An important premise in aquatic safety assessments is that if chronic no effect concentrations are not exceeded in the environment, then there will be no adverse ecological impact. The principles of testing recognize the fact that resources are limited and that every chemical and effluent cannot and need not be tested to the same comprehensive endpoint. Implicit in the application of these principles is the fact that it is impossible for us to be 100 percent correct in all our judgments, but with appropriate assessment techniques, we can be confident of being correct most of the time.

In the announcement of this workshop, it was stated that "while the agenda is focused on water discharges, the topics to be discussed are applicable to other areas, particularly the evaluation of new and existing chemicals under the Toxic Substances Control Act and for hazardous waste evaluation." It was also recognized that "one of the most difficult tasks

facing all of us today is the continued protection of the environment without unreasonable limitations of industrial growth and despite shrinking State and Federal resources." It is interesting to note that Region V personnel stated, "For industrial facilities with direct discharge to a waterway, we estimate that 95 percent do not need further water pollution control improvements to meet national and local requirements." For this audience of technical people and managers who must make decisions about the safety of chemicals and effluents, we should challenge ourselves to find, in the most cost effective manner possible, those five percent of the effluents that need additional attention. Similarly, we need to find the few chemicals out of the many thousands used that possess physical and biological properties likely to cause environmental problems.

At Monsanto, the Environmental Sciences group has been working for a number of years to (1) obtain the appropriate data base on the fate and effects of chemicals in the environment, (2) develop decision making concepts, and (3) develop new cost effective methods of obtaining the needed data. We came here today to learn what others are doing in structure activity relationships and to share our viewpoint on how to utilize some existing "tools," which we consider technically sound, to help identify those effluents and chemicals that must receive our resources to evaluate their aquatic safety. We will do this by demonstrating how some of the tools--like chemical structure, physical properties, and simple biological effects testing--can provide useful information at a minimum cost very early in a tiered approach to clearly identify potential problem chemicals and effluents.

BACKGROUND

Before getting into the details of the structure activity approach, it is useful and necessary to review some important basic principles of aquatic

hazard evaluation that were developed in the Pellston Workshop (1) and help govern our chemical and effluent program. They are:

- Aquatic chemical hazard is assessed by comparison of environmental exposure to biological effects.
- Exposure concentrations must be available, preferably measured, or at least predicted from physical properties and transformation rate data.
- Satisfactory methods for testing aquatic biological effects do exist.
- Data should be acquired in sequential tiers with decision points after each tier to (a) use or produce the chemical, (b) not use or produce the chemical, or (c) require additional testing before a decision can be made.

Table I shows the relationship between exposure and effects, giving the data necessary at each tier, and the hazard evaluation criteria needed for decision making. The basis of decision making is the ratio of the effect concentration to the exposure concentration which is called the safety margin. For example, if the safety margin is >1000 at the screening tier based upon estimated exposure concentrations and acute toxicity, further testing is probably not needed. A safety margin <1000 suggests that the environmental risk may be unacceptable and further testing is needed to demonstrate the safety of the chemical if production is planned. A graphical presentation of the same assessment process is shown in Figure 1. As a chemical evaluation program proceeds through the tiers and more data is collected, our confidence in our ability to make an accurate assessment increases. When the actual difference between exposure and effects concentration is small, it generally takes more data to accurately determine the safety margin. The decision point is moved toward later tiers. If the true difference between exposure and effects is very great, then acute toxicity data and a preliminary estimate of exposure may be enough to make a decision. In this case, the decision point can be moved up in time.

This concept emerged at an earlier workshop on Estimating the Hazard of Chemical Substances to Aquatic Life in 1977 (1) and has been widely accepted by the scientific community. Both industry and the EPA have relied upon these techniques in the administration of the Toxic Substances Control Act.

We at Monsanto believe that the time is near to expand the above conceptualization to include a "basic" tier based on physical properties to predict exposure and in the future to predict toxicity. We believe that there are many chemicals that do not need to enter the tier testing scheme. As noted in the introduction, this conference is designed to concentrate on those five percent of the effluents and chemicals with the highest probability of being a problem. We think this basic tier can help us set our priorities in testing programs. Figure 2 shows the same graph (without confidence intervals) with the exposure and effects lines extrapolated backwards. Theoretically, this means that through our current use of physical properties to predict exposure concentration and with continuing development in the ability of structure activity relationships to predict toxicity, we can add an earlier tier--i.e., "basic."

Structure activity relationships have been used for many years by pharmacologists in the drug industry to guide their efficacy and safety testing programs. Environmental toxicologists picked up some of the concepts for effects testing in the 1970s as evidenced in the Burlington Conference (2) and progress in this area continues to be made as demonstrated in the present workshop. At Monsanto, we view structure activity not on the primary level of the chemical configuration of molecules, but on the secondary level; that is, their physical properties. Although we certainly are interested in structural configuration on the theoretical level, we find that the science has not yet progressed to the point of being applicable on a day-to-day basis for a wide array of chemicals for

decision making. However, it is the summation of the chemical configuration, as reflected in physical properties, that represents the state-of-the-art science that is useful in our safety assessment programs. For instance, the recent work of Mackay (3) has been very significant in demonstrating how physical properties can be used to predict the distribution of chemicals in key environmental compartments: air, water, sediment, soil, and biota. By estimating the mass of each compartment, the level I model proposed by Mackay can be used to provide maximum estimates of environmental exposure concentrations for the various compartments.

Our safety assessment approach uses the Mackay level I model to provide early estimates of environmental exposure concentrations for purposes of selecting chemicals for additional testing (Figure 2). The confidence intervals are now extended into the basic tier and show an increase in confidence by the screening tier and, hence, an increase in our confidence to accurately assess the environmental safety of a chemical. Confidence intervals around the effects line have not been included because we are uncertain that state-of-the-art structure activity predictions have much utility to predict the toxic concentration of a chemical unless data are available in a homologous series.^R The cost of this tiered approach for assessing chemicals is shown in Figure 2. A rather dramatic increase in costs occurs proceeding through the tiers. The data obtained in the basic tier includes water solubility, vapor pressure, and volume of production. The cost of this tier is \$4,000. If no estimate of the acute toxicity is available, the cost of one acute toxicity test would have to be added, bringing the total cost to \$5,000. This is a significant savings compared to current costs for the screening tier. The cost of the screening tier is based upon our estimate of the cost of conducting the following tests: CO₂ evolution biodegradability, soil partition coefficient

and three acute aquatic toxicity tests. Similarly, cost estimates in the predictive and confirmative tiers are based upon projected costs of conducting additional acute, chronic and field toxicity tests as well as in-depth studies on transformation processes.

BASIC EXPOSURE TIER

The basic exposure tier has been added to provide an efficient and accurate means of selecting those key chemicals which need further testing. This is done by means of a safety factor analysis in the basic tier. Toxicity estimates are obtained from structure activity relationships for homologous series, the literature, or by conducting one acute aquatic toxicity test. Maximum environmental exposure concentrations are estimated using physical properties and Mackay's level I model. Chemicals with safety factors of 10,000 or less are considered for additional testing in the screening tier.

The use of physical properties to predict key environmental compartments where the mass of the chemical is most likely to partition is demonstrated for two homologous series of chemical; i.e., chlorinated benzenes and alkyl phthalate esters (Table 2). For both families, water solubility and vapor pressure decrease with increasing molecular weight. Conversely, the potential to partition to soil and fish (bioconcentration factor) increase with increasing molecular weight. However, the chlorinated benzenes and the phthalate esters have very different partitioning behavior. The chlorinated benzenes tend to partition to air, while the phthalate esters tend to partition to water. Within each homologous series, the "breakpoint" for tendency towards partitioning to sediments occurs between trichloro- and tetrachlorobenzene for the chlorinated benzenes and diethyl and di-N-butyl for the phthalates.

Examining the environmental partitioning and bioconcentration factors allows immediate "worst case" estimates, since persistence is not factored in

at the basic tier. A quick examination of the data for the 12 chemicals in Table 2 shows clearly that the product which would require the greatest effort would be hexachlorobenzene. Hexachlorobenzene does, in fact, appear to be widely spread throughout all environmental compartments and it also has a large predicted bioconcentration factor. Monitoring data has confirmed its presence in air, H₂O, sediments and biota (4).

Acute LC₅₀ data show unclear trends in toxicity for both the chlorobenzenes and phthalate esters. Part of the reason is that many LC₅₀ values exceed the water solubility of the product, and are, therefore, meaningless. Water solubility must be carefully considered when acute toxicity data is evaluated.

These partitioning data are used to suggest the type of testing that may be most appropriate. For the lower molecular weight benzenes, it is obvious that estimates of the rates of photolysis are needed. The phthalate esters would require an emphasis on aquatic water column effects testing. For the higher molecular weight chlorinated benzenes and phthalate esters, the sediments appear to be a significant compartment. Benthic invertebrate tests as well as aerobic and anaerobic sediment biodegradation studies may be appropriate. This approach provides us with a tool which can be used to determine where to maximize our environmental testing effort.

APPLICATION OF TIER CONCEPT TO EFFLUENTS

Effluents are complex mixtures of chemicals. We believe that it is logical to apply the tier approach which was developed for individual chemicals to effluents. The proposed application of the tier concept to effluents, like that for chemicals, is based upon the calculation of a safety margin in each tier. A decision is made in each tier as to the adequacy of the safety margin and whether the effluent is environmentally acceptable, unacceptable, or needs further testing (Table 3). Biological effects

testing is proposed for effluents similar to that currently being conducted with chemicals; i.e., acute, chronic and field toxicity tests as well as bioconcentration estimation and measurement and persistence testing. The environmental exposure concentration for effluents is not predicted from physical properties but rather it is calculated on the basis of the ratio of the volume of effluent to the volume of the receiving water; i.e., dilution capacity. This tier scheme is still in its infancy and will be provided as a "straw man" for discussion at a future EPA workshop (Wyoming, 1982).

Our schematic approach for assessing effluents includes the basic tier which is used to "screen out" those effluents which do not need to enter the tier scheme (Figure 3). The calculations for the basic tier are done prior to any actual testing. The dilution capacity of the receiving bodies of water is calculated and used to make an initial safety assessment for all effluents of interest. We propose that a dilution factor of 10,000 be used as a trigger for more testing. In other words, any effluent which is diluted $<10,000$ times is likely to be of higher environmental concern than one with a dilution factor $\geq 10,000$ and would, therefore, be tested in the screening tier. In proposing a dilution factor of 10,000 as a trigger for testing, we recognize that there is some dilution at which even the most toxic, most accumulative, and most persistent effluents will not have effects on aquatic organisms.

Experience has shown us that industrial effluent acute toxicity values are never less than 0.1 percent effluent and rarely less than 1.0 percent (LC_{50} of 0.1 percent diluted 10,000 times would result in no mortality in the receiving water with a safety factor of 10 for an acute exposure). By applying an application factor of 10 to estimate the chronic no effect concentration from the acute LC_{50} , it can be seen that for a worst case

situation, the margin of safety would be 1.0. This approach is not used to demonstrate conclusively that an effluent is environmentally acceptable, but rather as a sorting mechanism for identifying effluents which clearly need more testing.

We believe that in both the chemical and effluent tiers a demonstrated safety margin of 1.0 based on an extensive data base of acute and chronic toxicity tests and/or actual field testing is adequate to protect aquatic life. This conclusion is consistent with the water quality criteria methodology for deriving a chemical concentration in water which, if not exceeded, will allow for the survival and reproduction of aquatic species. The methodology in essence says chemical concentrations equal to or less than the water quality criterion are acceptable; i.e., a safety margin of 1.0 would, therefore, be acceptable.

SUMMARY

1. We are highly encouraged with the advances in the application of physical properties correlations to environmental distribution and exposure concentration predictions. We feel that this concept should be firmly placed within the tier approach for chemicals to set testing priorities.
2. We are uncertain about the use of structure-toxicity correlations outside of homologous chemical series at this time. Theoretically, as structure-activity estimation techniques are validated with a much larger data base, carefully constructed to eliminate poor data or LC₅₀ values greater than water solubility, this may be possible in the future.
3. We feel that the tier concept provides a sound philosophical base for use with effluents. It is consistent with present techniques for assessing chemicals and focuses our efforts on the margin of safety for organisms in the receiving stream rather than on numerical constructs such as BAT

(Best Available Technology) compliance or end of the pipe LC₅₀ values which have no bearing on the well being of the organisms themselves.

In summary, the critical question asked at the beginning of this presentation is how much testing is needed to better satisfy regulators, citizens, environmentalists and producers that chemicals and effluents are not harmful? There is no set answer. We recognize in today's society not every chemical can and should be tested to the same extent. Efficient and dependable methods for screening out those chemicals which need not be tested is a must. It has been stated that 95 percent of industrial facilities do not need additional pollution control. We, at Monsanto, agree with this and also believe that the majority of the chemicals being produced present little or no harm to the environment. We have spent considerable time and effort in developing, first, hazard methodology and, secondly, effluent assessment techniques. Both procedures are designed to protect the environment through the use of appropriate safety margins and maximize the use of minimum data bases for screening chemicals and effluents in order to make decisions concerning safety as early as possible in a tier testing program.

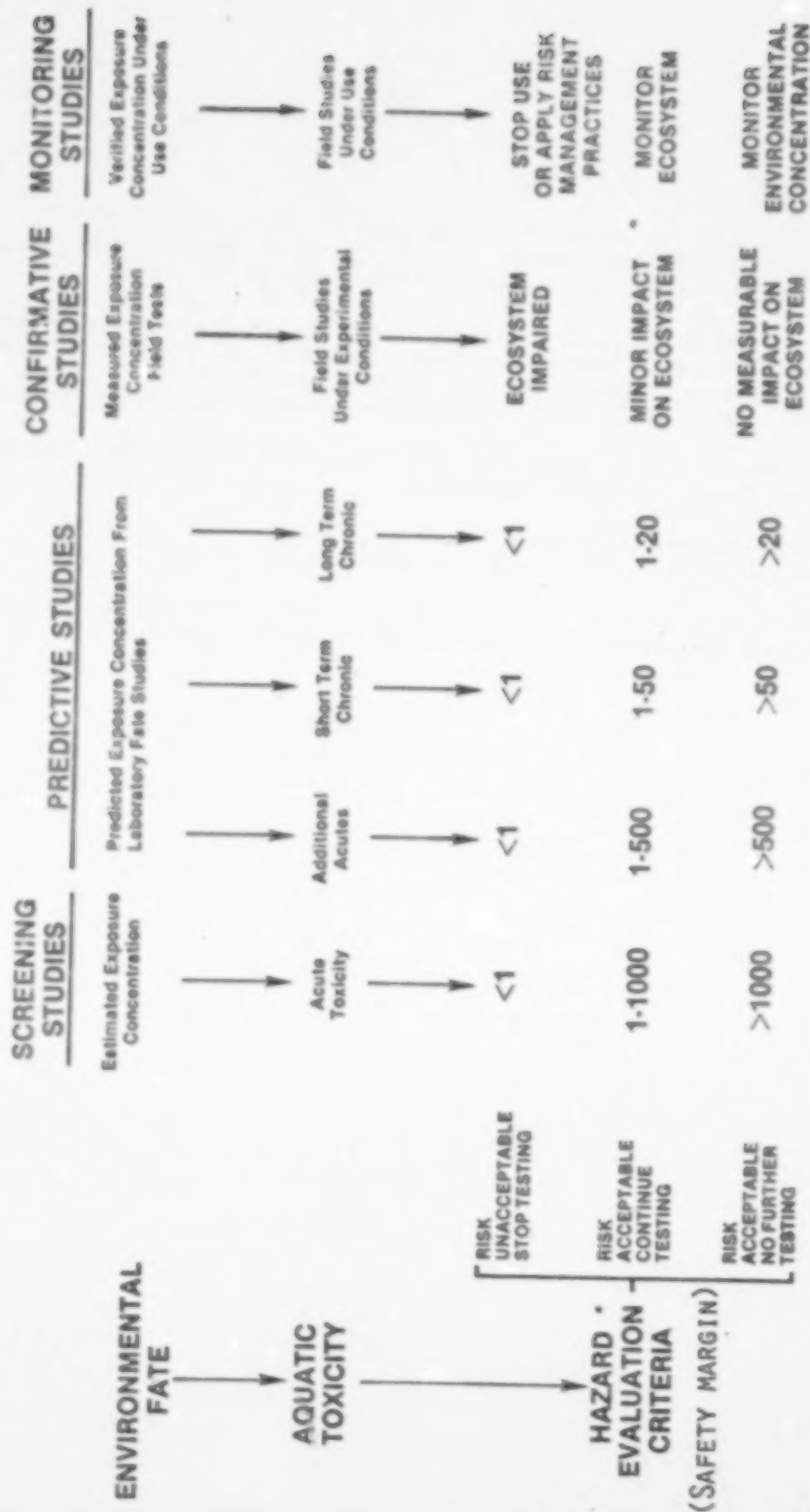
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TABLE 1. HAZARD EVALUATION PROCESS FOR ASSESSING THE ENVIRONMENTAL SAFETY OF CHEMICALS TO AQUATIC ORGANISMS.

HAZARD EVALUATION PROCESS



* SAFETY MARGIN IS CALCULATED BY DIVIDING THE TOXIC EFFECT CONCENTRATION BY THE EXPOSURE CONCENTRATION.

FIGURE 1

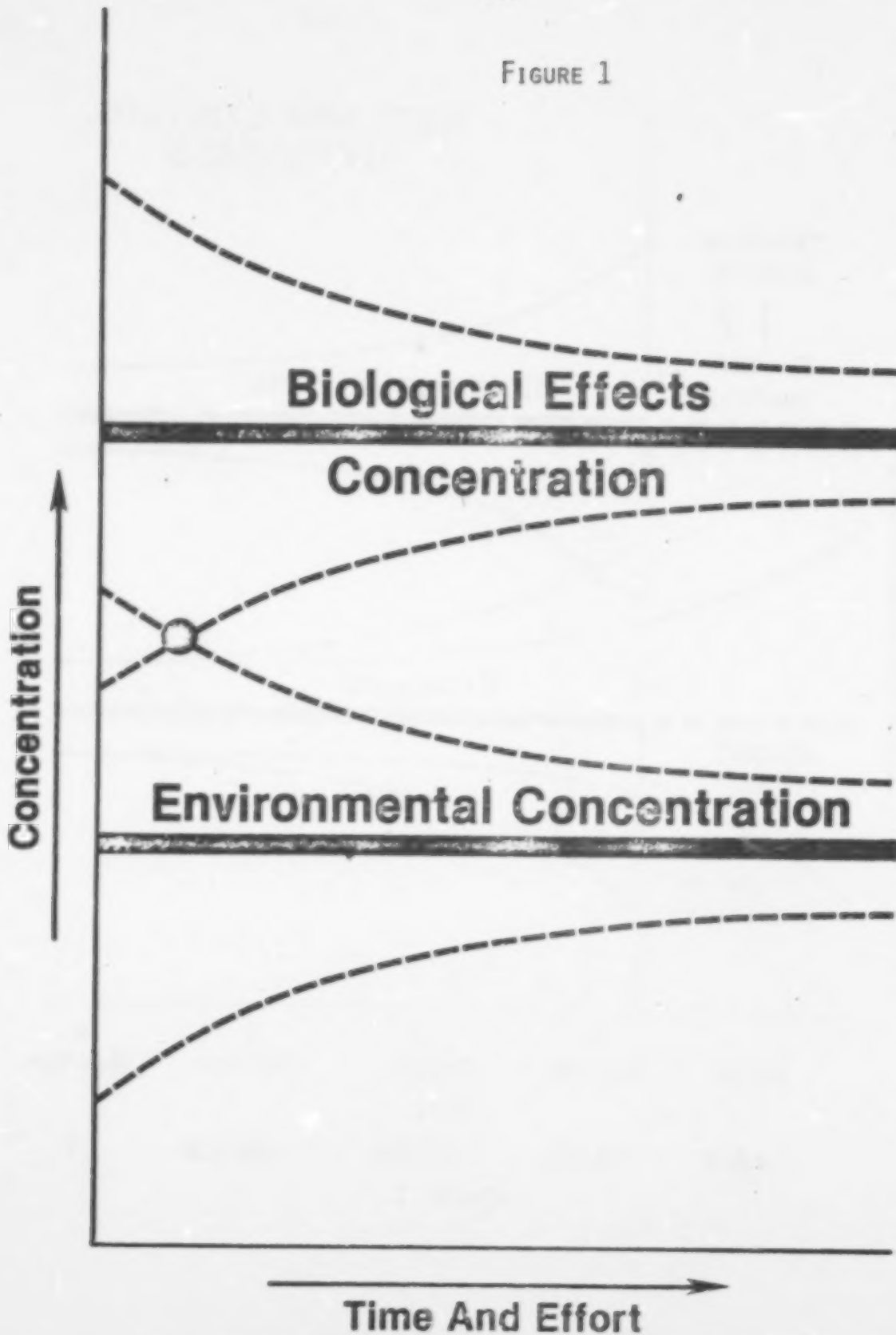


FIGURE 2

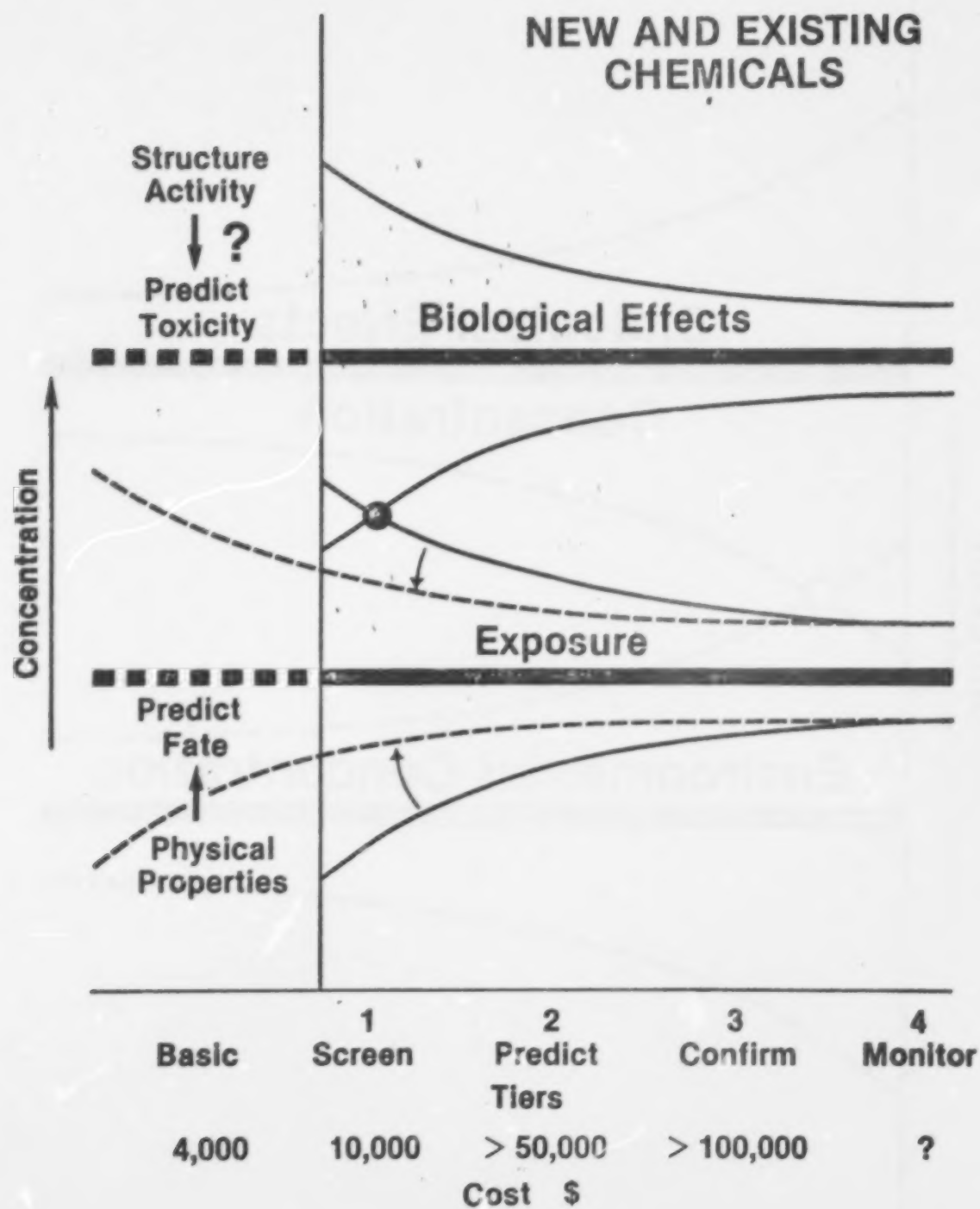
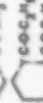


TABLE 2. GENERAL RELATIONSHIPS BETWEEN CHEMICAL STRUCTURE, PHYSICAL PROPERTIES, ENVIRONMENTAL PARTITIONING, BIOCONCENTRATION AND ACUTE TOXICITY OF SOME CHLORINATED BENZENES AND PHTHALATE ESTERS.

CHEMICAL		Physical Properties				Environmental Partitioning %				Bioconcentration Factor	Acute LC50 mg/l	
		MW	WS	VP	Kp	Air	Water	Soil	Sediment		Daphnia	Bluegill
Chlorinated Benzenes												
Benzene		78	1780	95.2	0.10	99.7	0.3	0	0	13	203	22
Monochloro		113	500	8.8	0.37	99.3	0.7	0	0	30	86	16
Dichloro		147	145	1.5	1.2	99.0	0.8	0	0.02	120	2.4	5.6
Trichloro		181	30	0.4	4.8	97.7	0.5	0.3	1.5	195	50	3.4
Tetrachloro		216	6	~10 ⁻³	19.6	82.3	12.4	1.1	4.3	474	530	1.6
Pentachloro		250	0.14	~10 ⁻⁴	416	66.3	3.5	5.4	24.6	3331	5.3	0.2
Hexachloro		285	0.006	~10 ⁻⁶	5410	23.1	0.6	13.2	63.1	18,000	—	12.0
Phthalate Esters												
Phthalic Anhydride		148	6200	~10 ⁻³	0.06	0.2	99.8	0	0	12	> 100	—
DiMethyl		194	4320	~10 ⁻³	0.11	0.3	99.4	0	0.2	16	33	50
DiEthyl		222	896	~10 ⁻⁴	0.40	0.8	98.1	0.2	0.7	36	52	96
Di-N-Butyl		278	13	~10 ⁻⁶	13.1	1.3	76.6	4.0	18	368	~7	0.7
Di(2-Ethyl-Hexyl)		391	1.3	~10 ⁻⁷	103	0.1	30.4	12.2	57.3	1402	2	> 10

¹ Physical properties are molecular weight (MW), water solubility ppm (WS), vapor pressure torr (VP), sediment/water partition factor (Kp).

² Environmental partitioning calculated (Ref. 3).

³ Bioconcentration calculated from water solubility (Ref. 4).

FIGURE 3

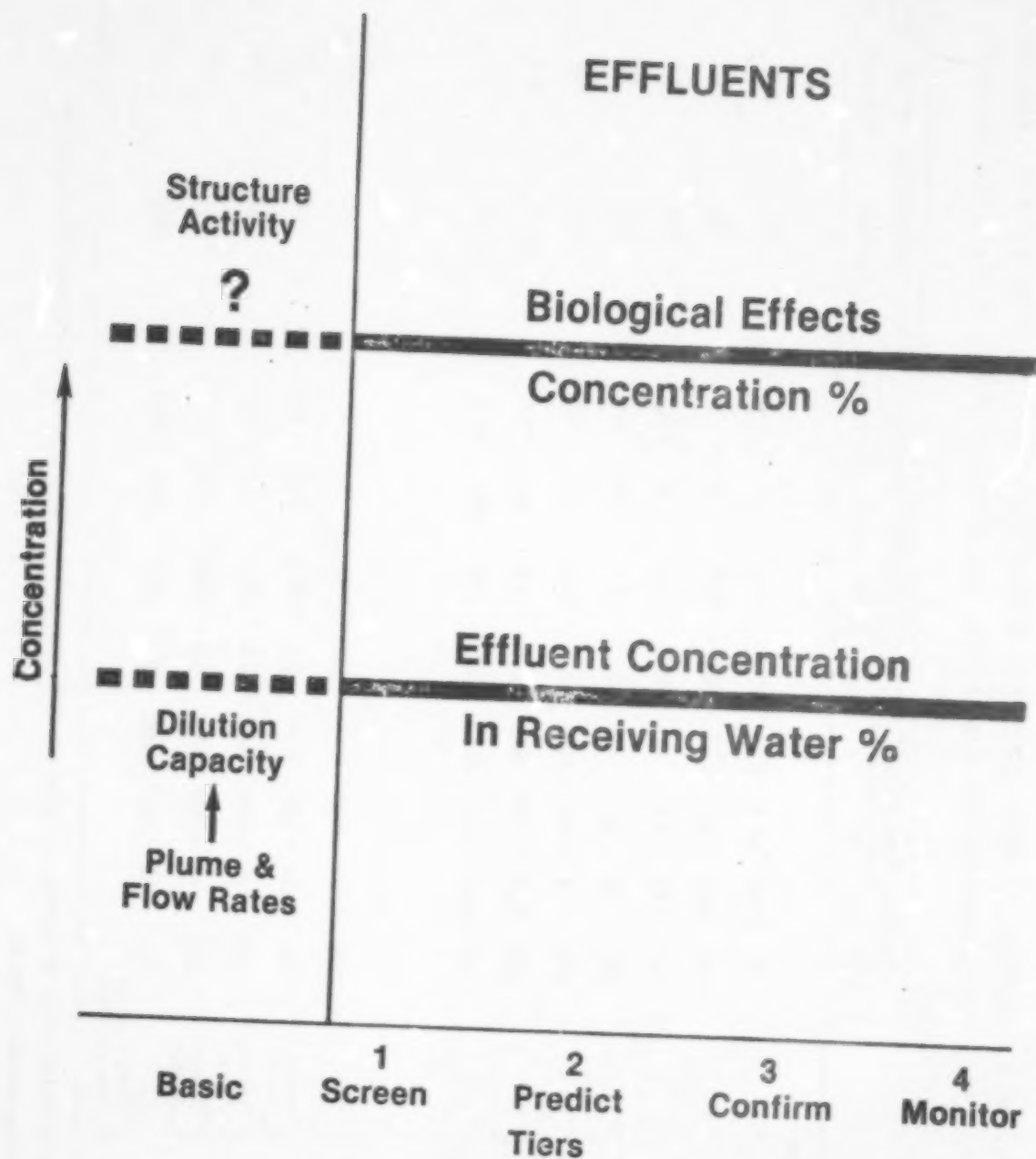


TABLE 3. EXPANDED TIER APPROACH FOR ASSESSING THE SAFETY OF CHEMICALS AND EFFLUENTS BASED ON SAFETY MARGINS.

TIERS

<u>CHEMICAL</u>	<u>BASIC</u>	<u>SCREEN</u>	<u>PREDICT</u>	<u>CONFIRM</u>	<u>MONITOR</u>
Effect	Structure Activity ?	Acute	Acute Chronic	Field Ecosystem	Ecosystem
Exposure	Physical Properties Prediction	Predict Concentration Model	Improve Prediction	Measure	Verify
Safety Margin	—	1,000	500-20	20-1	1

<u>EFFLUENT</u>	<u>BASIC</u>	<u>SCREEN</u>	<u>PREDICT</u>	<u>CONFIRM</u>	<u>MONITOR</u>
Effect	Structure Activity ?	Acute	Acute Chronic	Site Visit Acute Chronic	Ecosystem Field Study
Exposure	Dilution Capacity 10,000	Effluent % Concentration	Effluent % Concentration	Plume Study Zones Of Impact	Field Study
Safety Margin	—	1,000	100-10	10-1	1

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IDENTIFICATION, EVALUATION AND CONTROL OF TOXIC SUBSTANCES IN INDUSTRIAL EFFLUENTS

JUNE 15-16, 1982

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